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filled with particles 924 such that the countershape may be conveniently shaped to conform to the shape of face 906 or face 907. In an embodiment, the countershape is preferably a "beanbag" that contains particles 924 and may be conformable to the shape of a mold face placed on top of it. Particles 924 may include ceramic material, metal material, glass beads, sand and/or salt. The particles preferably facilitate conductive heat to be applied to face 906 or face 907 substantially evenly.

In an embodiment, the countershape 920 is preferably placed on top of heat source 418. Countershape 920 is preferably heated until the temperature of the countershape is substantially near or equal to the temperature of the surface of the heat source. The countershape may then be "flipped over" such that the heated portion of the countershape that has a temperature substantially near or equal to that of the surface of the heat source is exposed. A mold may be placed on top of the heated portion of the countershape, and the countershape is preferably conformed to the shape of the face of the mold. In this manner, the rate of conductive heat transfer to the lens may begin at a maximum. Heat is preferably conductively transferred through the countershape and the mold face to a face of the lens. The temperature of the heated portion of the countershape may tend to decrease after the mold is placed onto the countershape.

In an embodiment, heat distributor 910 may partially insulate a mold member from conductive heat source 418. The heat distributor preferably allows a gradual, uniform transfer of heat to the mold member. The heat distributor is preferably made of rubber and/or another suitable material. The heat distributor may include countershapes of various shapes (e.g., hemispherically concave or convex) and sizes that may be adapted to contact and receive mold members.

In an embodiment, heat may be conductively applied by the heat source to only one outside face of one mold member. This outside face may be face 906 or face 907. Heat may be applied to the back face of the lens to enhance crosslinking and/or tintability

of the lens material proximate to the surface of the back face of the lens.

In a preferred embodiment, a thermostatically controlled hot plate 418 is preferably used as a heat source. Glass optical mold 928 is preferably placed convex side up on hot plate 418 to serve as a countershape. The glass optical mold preferably has about an 80 mm diameter and a radius of curvature of about 93mm. Rubber disc 929 may be placed over this mold 928 to provide uniform conductive heat to the lens mold assembly. The rubber disc is preferably made of silicone and preferably has a diameter of approximately 74 mm and a thickness of about 3 mm. The lens mold assembly is preferably placed on mold 928 so that outside face 906 of a mold member of the assembly rests on top of mold 928. It is preferred that the edge of the lens mold assembly not directly contact the hot plate. The lens mold assembly preferably receives heat through the rubber disc and not through its mold edges.

To achieve good yield rates and reduce the incidence of premature release while using the conductive heat method, it may be necessary for the edge of the lens to be completely cured and dry before conductive heat is applied. If the lens edge is incompletely cured (i.e., liquid or gel is still present) while conductive heat is applied, there may be a high incidence of premature release of the lens from the heating unit.

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In an embodiment, the edges of a lens may be treated to cure or remove incompletely cured lens forming material (see above description) before conductive heat is applied. The mold cavity may be defined by at least gasket 908, first mold member 902, and second mold member 904. Activating light rays may be directed toward at least one of the mold members, thereby curing the lens forming material to a lens preferably having front face 916, a back face 915, and edges. Upon the formation of the lens, the gasket may be removed from the mold assembly. An oxygen barrier may be used to cure any remaining liquid or gel on the lens edge as described in more detail below. An oxygen barrier treated with photoinitiator is preferably employed. Alternatively, any

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remaining liquid or gel may be removed manually. Once the edge of the lens is dry, a face of the lens may be conductively heated using any of the methods described herein.

In an embodiment, a lens may be tinted after receiving conductive heat postcure treatment in a mold cavity. During tinting of the lens, the lens is preferably immersed in a dye solution.

The operation of the lens curing system may be controlled by a microprocessor based controller 50 (Fig. 1). Controller 50 preferably controls the operation of coating unit 20, lens curing unit 30, and post-cure unit 40. Controller 50 may be configured to substantially simultaneously control each of these units. In addition, the controller may include a display 52 and an input device 54. The display and input device may be configured to exchange information with an operator.

Controller 50 preferably controls a number of operations related to the process of forming a plastic lens. Many of the operations used to make a plastic lens (e.g., coating, curing and post-cure operations) are preferably performed under a predetermined set of conditions based on the prescription and type of lens being formed (e.g., ultraviolet/visible light absorbing, photochromic, colored, etc.). Controller 50 is preferably programmed to control a number of these operations, thus relieving the operator from having to continually monitor the apparatus.

In some embodiments, the lens or mold members may be coated with a variety of coatings (e.g., a scratch resistant or tinted coating). The application of these coatings may require specific conditions depending on the type of coating to be applied.

Controller 50 is preferably configured to produce these conditions in response to input from the operator.

When a spin coating unit is used, controller 50 may be configured to control the

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rotation of the lens or mold member during the coating process. Controller 50 is preferably electronically coupled to the motor of the spin coating unit. The controller may send electronic signals to the motor to turn the motor on and/or off. In a typical coating process the rate at which the mold or lens is rotated is preferably controlled to achieve a uniform and defect free coating. The controller is preferably configured to control the rate of rotation of the mold or lens during a curing process. For example, when a coating material is being applied, the mold or lens is preferably spun at relatively high rotational rates (e.g., about 900 to about 950 RPM). When the coating material is being cured, however, a much slower rotational rate is preferably used (e.g., about 200 RPM). The controller is preferably configured to adjust the rotational rate of the lens or mold depending on the process step being performed.

The controller is also preferably configured to control the operation of lamps 24. The lamps are preferably turned on and off at the appropriate times during a coating procedure. For example, during the application of the coating material activating lights are typically not used, thus the controller may be configured to keep the lamps off during this process. During the curing process, activating light may be used to initiate the curing of the coating material. The controller is preferably configured to turn the lamps on and to control the amount of time the lamps remain on during a curing of the coating material. The controller may also be configured to create light pulses to affect curing of the coating material. Both the length and frequency of the light pulses may be controlled by the controller.

The controller is also preferably configured to control operation of the lens-curing unit. The controller may perform some and/or all of a number of functions during the lens curing process, including, but not limited to: (i) measuring the ambient room temperature; (ii) determining the dose of light (or initial dose of light in pulsed curing applications) required to cure the lens forming composition, based on the ambient room temperature; (iii) applying the activating light with an intensity and duration sufficient to

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equal the determined dose; (iv) measuring the composition's temperature response during and subsequent to the application of the dose of light; (v) calculating the dose required for the next application of activating light (in pulsed curing applications); (vi) applying the activating light with an intensity and duration sufficient to equal the determined second dose; (vii) determining when the curing process is complete by monitoring the temperature response of the lens forming composition during the application of activating light; (viii) turning the upper and lower light sources on and off independently; (ix) monitoring the lamp temperature, and controlling the temperature of the lamps by activating cooling fans proximate the lamps; and (x) turning the fans on/off or controlling the flow rate of an air stream produced by a fan to control the composition temperature. Herein, "dose" refers to the amount of light energy applied to an object, the energy of the incident light being determined by the intensity and duration of the light.

A temperature monitor may be located at a number of positions within the lens curing unit 30. In one embodiment an infra-red temperature sensor may be located such that it may measure the temperature of the mold and/or the lens forming composition in the mold cavity. One infra-red temperature sensor may be the Cole-Parmer Model E39669-00 (Vernon Hills, Illinois).

The temperature monitor may measure the temperature within the chamber and/or the temperature of air exiting the chamber. The controller may be configured to send a signal to a cooler and/or distributor to vary the amount and/or temperature of the cooling air. The temperature monitor may also determine the temperature at any of a number of locations proximate the mold cavity. The temperature monitor preferably sends a signal to the controller such that the temperature of the mold cavity and/or the lens forming composition may be relayed to the controller throughout the curing process.

During the initial set-up of a curing process the temperature of the lens forming composition within the mold cavity may be determined. This initial temperature of the

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lens forming composition may be about equal to the ambient room temperature. The controller may then determine the initial temperature of the lens forming composition by measuring the ambient room temperature. Alternatively, the initial temperature of the lens forming composition may be measured directly using the aforementioned temperature sensors.

The controller preferably determines the initial dose to be given to the lens forming composition based on the initial temperature of the composition. The controller may use a table to determine the initial dose, the table including a series of values correlating the initial temperature to the initial dose and/or the mass of the lens forming composition. The table may be prepared by routine experimentation. To prepare the table a specific lens forming composition of a specific mass is preferably treated with a known dose of activating light. The mold cavity is preferably disassembled and the gelation pattern of the lens forming composition observed. This procedure may be repeated, increasing or decreasing the dosage as dictated by the gelation patterns, until the optimal dosage is determined for the specific lens forming composition.

During this testing procedure the initial temperature of the lens forming composition may be determined, this temperature being herein referred to as the "testing temperature". In this manner, the optimal dose for the lens forming composition at the testing temperature may be determined. When the lens forming material has an initial temperature that is substantially equal to the testing temperature, the initial dosage may be substantially equal to the experimentally determined dosage. When the lens forming material has a temperature that is substantially greater or less than the testing temperature, the initial dose may be calculated based on a function of the experimentally determined initial dose. In single dose applications the initial dose of activating light will be sufficient to substantially cure the plastic lens. For multi-pulse applications, the initial dose will be followed by additional light doses.

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In an embodiment, the controller is preferably adapted to control the intensity and duration of activating light pulses delivered from the activating light source and the time interval between the pulses. The activating light source may include a capacitor which stores the energy required to deliver the pulses of activating light. The capacitor may allow pulses of activating light to be delivered as frequently as desired. A light sensor may be used to determine the intensity of activating light emanating from the source. The light sensor is preferably adapted to send a signal to the controller, which is preferably adapted to maintain the intensity of the activating light at a selected level. A filter may be positioned between the activating light source and the light sensor and is preferably adapted to inhibit a portion of the activating light rays from contacting the light sensor. This filter may be necessary to keep the intensity of the activating light upon the light sensor within the detectable range of the light sensor.

In an embodiment, a shutter system may be used to control the application of activating light rays to the lens forming material. The shutter system preferably includes air-actuated shutter plates that may be inserted into the curing chamber to prevent activating light from reaching the lens forming material. The shutter system may be coupled to the controller, which may actuate an air cylinder to cause the shutter plates to be inserted or extracted from the curing chamber. The controller preferably allows the insertion and extraction of the shutter plates at specified time intervals. The controller may receive signals from temperature sensors allowing the time intervals in which the shutters are inserted and/or extracted to be adjusted as a function of a temperature of the lens forming composition and/or the molds. The temperature sensor may be located at numerous positions proximate the mold cavity and/or casting chamber.

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Alternatively, the shutter system may include an LCD filter that may be darkened to inhibit the activating light from reaching the lens forming material. The controller is preferably configured to darken the LCD panel at specified time intervals. The controller may receive signals from temperature sensors allowing the time intervals

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in which the LCD panel is darkened to be adjusted as a function of a temperature of the lens forming composition and/or the molds.

In an embodiment, a single dose of activating light may be used to cure a lens forming composition. The controller may monitor the change in temperature of the lens forming composition during the application of activating light. The activating light preferably initiates a polymerization reaction such that the temperature of the lens forming composition begins to rise. By monitoring the change in temperature over a time period the controller may determine the rate of temperature change. The controller preferably controls the polymerization of the lens forming composition based on the rate of temperature change. When the temperature is found to be rising at a faster than desired rate, the desired rate being determined based on previous experiments, the temperature controller may alter the intensity and/or the duration of the pulse such that the rate of temperature change is lowered. The duration of the activating light may be shortened and/or the intensity of the activating light may be diminished to achieve this effect. The controller may also increase the rate of cooling air blowing across the mold to help lower the temperature of the lens forming composition. Alternatively, if the temperature of the reaction is increasing too slowly, the controller may increase the intensity of the activating light and/or increase the duration of the pulse. Additionally, the controller may decrease the rate of cooling air blowing across the mold to allow the temperature of the lens forming composition to rise at a faster rate.

One manner in which the temperature may be controlled is by monitoring the temperature during the application of activating light, as described in U.S. Patent No. 5,422,046 to Tarshiani, et al. During activating light irradiation, the temperature of the lens forming composition tends to rise. When the temperature reaches a predetermined upper set point the activating light source is preferably turned off. Removal of the activating energy may allow the temperature to gradually begin to fall. When the temperature is reduced to a predetermined lower set point the activating light source is

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preferably turned on. In this manner, the temperature may be controlled within a desired range. This temperature range tends to be very broad due to the nature of the lens forming polymerization reactions. For example, turning the activating light off at a predetermined upper set point may not insure that the temperature of the lens forming composition will stop at that point. In fact, it is more likely that the temperature may continue to rise after the upper set point has been reached. To offset this effect the upper set point may be set at a temperature lower than the upper temperature desired during the lens forming process. Such a method of temperature control may be insufficient to control the temperature. As shown in Fig. 17, increase in the temperature of a lens forming composition during the lens forming process may not be constant. Since the increase in temperature of the composition changes as the process continues, the use of an upper set point for controlling the temperature may not adequately prevent the composition from reaching greater than desired temperatures. Additionally, near the completion of the process the upper set point may be set too low, thereby preventing the lens forming composition from reaching a temperature that is adequate to maintain the polymerization reaction due to insufficient doses of activating light.

In an embodiment the temperature control process may be described as a modified Proportional-Integral-Derivative ("PID") control method. Preferably, the controller is configured to operate the lens-curing system using a PID control method. The controller may use a number of factors to determine the dose of activating light applied for each pulse. The controller preferably measures the temperature as well as the rate of temperature change.

The PID control method involves the combination of proportional, integral and derivative controlling methods. The first, proportional control, may be achieved by mixing two control factors in such a way as to achieve the desired effect. For lens control the two factors which tend to have the most effect on temperature control may be the dosage of activating light and the flow rate of the cooling air. These two factors may be

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altered to achieve a desired temperature response. If the temperature must be raised as rapidly as possible a full dosage of light may delivered with no cooling air present. Similarly, if the composition must be rapidly cooled the sample may be treated with cooling air only. Preferably the two factors, application of incident light and cooling, are preferably both applied to achieve the desired temperature response. The mixture, or proportions of these factors may allow the temperature of the composition to be controlled.

The use of proportional control tends to ignore other effects that influence the temperature of the lens forming composition. During the lens forming process, the temperature of the lens forming composition may vary due to the rate of polymerization of the reaction. When the composition is undergoing a rapid rate of polymerization, the temperature of the composition may rise beyond that determined by the proportional setting of the activating light and cooling air controls. Toward the end of the process the lens may become too cool due to the a reduction in the rate of polymerization of the composition. The use of proportional control may therefore be inadequate to control this procedure and may lead to greater than desired variations in the temperature of the composition.

These limitations may be overcome by altering the proportions of the two components in response to the temperature of the composition. A single set point may be used to control the temperature of a reaction. As the temperature rises above this set point the proportion of the activating light and cooling may be adjusted such that the temperature begins to lower back toward the set point. If the temperature drops below the set point the proportion of activating light and cooling may be adjusted to raise the temperature back to the set point. Typically, to lower the temperature the dose of activating light may be reduced and/or the flow rate of the cooling air may be increased. To raise the temperature the dose of activating light may be increased and/or the flow rate of the cooling air may be decreased.

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The use of proportional control in this manner may not lead to a steady temperature. Depending on the set point and the response time of the lens forming composition to variations in the dosage of light and/or cooling air, the temperature may oscillate over the set point, never attaining a steady value. To better control such a system the rate of change of the temperature over a predetermined time period is preferably monitored. As the temperature rises the rate at which the temperature rises is preferably noted. Based on this rate of change the controller may then alter the dosage of activating light and/or cooling air such that a temperature much closer to the set point may be achieved. Since the rate will change in response to changes in the rate of polymerization, such a system may better control the temperature of the lens forming composition throughout the process.

In an embodiment, the controller may be a modified PID controller or a computer programmed to control the lens curing unit using a PID control scheme. The controller preferably monitors the temperature of the lens forming composition throughout the process. Additionally, the controller may monitor the rate of change of temperature throughout the reaction. When a plurality of pulses are being applied to control the polymerization, the controller preferably controls the duration and intensity of each pulse to control the temperature of the composition. In a typical process the rate of change in temperature is preferably monitored after the application of an activating light pulse. If the temperature is trending in an upward direction, the controller preferably waits for the temperature to crest and start descending, before the application of additional light pulses. This cresting temperature may vary, as depicted in Fig. 17, throughout the lens forming process. After the temperature has passed a predetermined set point, a dose, calculated from the rate of change in temperature caused by the application of the previous pulse, may be applied to the lens forming composition. After the light pulse is delivered the controller may repeat the procedure additional times.

When the reaction nears completion the controller detects the lack of response to the last exposure (i.e. the lens temperature did not increase appreciably). At this point the controller may apply a final dose to assure a substantially complete cure and notify the operator that the mold assembly is ready to be removed form the chamber.

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One method of controlling the dose of light reaching the lens may be through the use of filters, as described above. In one embodiment, an LCD filter system may be used to adjust the intensity of incoming light. The LCD system is preferably coupled to the controller such that a pattern displayed by the LCD system may be altered by the controller. The controller preferably configures the pattern of light and dark areas on the LCD panel such that light having the optimal curing intensity pattern hits the mold assemblies. The pattern that is produced is preferably based on the prescription and type of lens being produced.

In another embodiment, the controller may actively change the pattern on the LCD panel during a curing cycle. For example, the pattern of light and dark regions may be manipulated such that the lens is cured from the center of the lens then gradually expanded to the outer edges of the lens. This type of curing pattern may allow a more uniformly cured lens to be formed. In some instances, curing in this manner may also be used to alter the final power of the formed lens.

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In another embodiment, the LCD panel may be used as a partial shutter to reduce the intensity of light reaching the lens assembly. By blackening the entire LCD panel the amount of light reaching any portion of the mold assembly may be reduced. The controller may be configured to cause the LCD panel to create "pulses" of light by alternating between a transmissive and darkened mode. By having the LCD panel create these light "pulses" the need for a flash ballast or similar pulse generating equipment may be unnecessary. Thus the use of a controller and an LCD panel may simplify the system.

In some embodiments, the lens may require a post-curing process. The post-cure process may require specific conditions depending on the type of lens being formed. The controller is preferably configured to produce these conditions in response to input from the operator.

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The controller is preferably configured to control the operation of lamps 440 (See Fig. 12). The lamps are preferably turned on and off at the appropriate times during the post-cure procedure. For example, in some post-cure operations the lights may not be required, thus the controller would keep the lights off during this process. During other processes, the lights may be used to complete the curing of the lens. The controller is preferably configured to turn the lights on and to control the amount of time the lights remain on during a post-cure procedure. The controller may also be configured to create light pulses during the post-cure procedure. Both the length and frequency of the light pulses may be controlled by the controller.

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The controller is preferably configured to control operation of the heating device 418 during the post-cure operation. Heating device 418 is preferably turned on and off to maintain a predetermined temperature within the post-cure unit. Alternatively, when a resistive heater is used, the current flow through the heating element may be altered to control the temperature within the post-cure unit. Preferably both the application of light and heat are controlled by the controller. The operation of fans, coupled to the post-cure unit, is also preferably controlled by the controller. The fans may be operated by the controller to circulate air within or into/out of the post-cure unit.

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Additionally, the controller may provide system diagnostics to determine if the system is operating properly. The controller may notify the user when routine maintenance is due or when a system error is detected. For example, the controller may monitor the current passing through lamps of the coating, lens curing, or post-cure unit to determine if the lamps are operating properly. The controller may keep track of the

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number of hours that the lamps have been used. When a lamp has been used for a predetermined number of hours a message may be transmitted to an operator to inform the operator that the lamps may require changing. The controller may also monitor the intensity of light produced by the lamp. A photodiode may be placed proximate the lamps to determine the intensity of light being produced by the lamp. If the intensity of light falls outside a predetermined range, the current applied to the lamp may be adjusted to alter the intensity of light produced (either increased to increase the intensity; or decreased to decrease the intensity). Alternatively, the controller may transmit a message informing the operator that a lamp needs to be changed when the intensity of light produced by the lamp drops below a predetermined value.

The controller may also manage an interlock system for safety and energy conservation purposes. If the lens drawer assembly from the coating or post-cure units are open the controller is preferably configured to prevent the lamps from turning on. This may prevent the operator from inadvertently becoming exposed to the light from the lamps. Lamps 24 for the coating unit 20 are preferably positioned on cover 22 (See Fig. 1). In order to prevent inadvertent exposure of the operator to light from lamps 24 a switch is preferably built into the cover, as described above. The controller is preferably configured to prevent the lamps 24 from turning on when the cover is open. The controller may also automatically turn lamps 24 off if the cover is opened when the lenses are on. Additionally, the controller may conserve energy by keeping fans and other cooling devices off when the lamps are off.

The controller may also be configured to interact with the operator. The controller preferably includes an input device 54 and a display screen 52. The input device may be a keyboard (e.g., a full computer keyboard or a modified keyboard), a light sensitive pad, a touch sensitive pad, or similar input device. A number the parameters controlled by the controller may be dependent on the input of the operator. In the initial set up of the apparatus, the controller may allow the operator to input the type of lens

being formed. This information may include type of lens (clear, ultraviolet absorbing, photochromic, colored, etc.), prescription, and type of coatings (e.g., scratch resistant or tint).

Based on this information the controller is preferably configured to transmit information back to the operator. The operator may be instructed to select mold members for the mold assembly. The mold members may be coded such that the controller may indicate to the operator which molds to select by transmitting the code for each mold member. The controller may also determine the type of gasket required to properly seal the mold members together. Like the mold members, the gaskets may also be coded to make the selection of the appropriate gasket easier.

The lens forming compositions may also be coded. For the production of certain kinds of lenses a specific lens forming composition may be required. The controller may be configured to determine the specific composition required and transmit the code for that composition to the operator. The controller may also signal to the operator when certain operations need to be performed or when a particular operation is completed (e.g., when to place the mold assembly in the lens curing unit, when to remove the mold assembly, when to transfer the mold assembly, etc.).

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Referring now to Fig. 38, another embodiment of a plastic lens curing apparatus is generally indicated by reference numeral 1000. As shown in Fig. 38, lens forming apparatus 1000 includes at least one coating unit 1020, a pair of stacked lens curing units 1030 and 1035, a post-cure unit 1040, and a controller 1050. Preferably, apparatus 1000 includes two coating units 1020. Coating unit 1020 is preferably configured to apply a coating layer to a mold member or a lens. Preferably, coating unit 1020 is a spin coating unit. Each of the lens curing units, 1030 and 1035, includes an activating light source for producing activating light. The activating light source is preferably configured to direct light toward a mold assembly. Post-cure unit 1040 is preferably configured to complete

the polymerization of partially cured plastic lenses. Post-cure unit 1040 preferably includes an activating light source and a heat source. Controller 1050 is preferably a programmable logic controller. Controller 1050 is preferably coupled to coating units 1020, lens curing units 1030 and 1035, and post-cure unit 1040, such that the controller may be capable of substantially simultaneously operating the four units 1020, 1030, 1035 and 1040. Controller 50 may be a computer. During the production of plastic lenses the lens curing step may be the most time consuming part of the process. By adding additional curing units to the system the throughput of the system may be increased, allowing the operator to form more lenses in a given time period.

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LENS FORMING COMPOSITIONS

The lens forming material may include any suitable liquid monomer or monomer mixture and any suitable photosensitive initiator. As used herein "monomer" is taken to mean any compound capable of undergoing a polymerization reaction. Monomers may include non-polymerized material or partially polymerized material. When partially polymerized material is used as a monomer, the partially polymerized material preferably contains functional groups capable of undergoing further reaction to form a new polymer. The lens forming material preferably includes a photoinitiator that interacts with activating light. In one embodiment, the photoinitiator absorbs ultraviolet light having a wavelength in the range of 300 to 400 nm. In another embodiment, the photoinitiator absorbs actinic light having a wavelength in the range of about 380 nm to 490 nm. The liquid lens forming material is preferably filtered for quality control and placed in the lens molding cavity 382 by pulling the annular gasket 380 away from one of the opposed mold members 378 and injecting the liquid lens forming material into the lens molding cavity 382 (See Fig. 11). Once the lens molding cavity 382 is filled with such material, the annular gasket 380 is preferably replaced into its sealing relation with the opposed mold members 378.

Those skilled in the art will recognize that once the cured lens is removed from the lens molding cavity 382 by disassembling the opposed mold members 378, the lens may be further processed in a conventional manner, such as by grinding its peripheral edge.

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A polymerizable lens forming composition includes an aromatic-containing bis(allyl carbonate)-functional monomer and at least one polyethylenic-functional monomer containing two ethylenically unsaturated groups selected from acrylyl or methacrylyl. In a preferred embodiment, the composition further includes a suitable photoinitiator. In other preferred embodiments, the composition may include one or more polyethylenic-functional monomers containing three ethylenically unsaturated groups selected from acrylyl or methacrylyl, and a dye.

Aromatic-containing bis(allyl carbonate)-functional monomers include bis(allyl carbonates) of dihydroxy aromatic-containing material. The dihydroxy aromatic-containing material from which the monomer is derived may be one or more dihydroxy aromatic-containing compounds. Preferably the hydroxyl groups are attached directly to nuclear aromatic carbon atoms of the dihydroxy aromatic-containing compounds. The monomers are themselves known and may be prepared by procedures well known in the art.

The aromatic-containing bis(allyl carbonate)-functional monomers may be represented by the formula:

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in which A_1 is the divalent radical derived from the dihydroxy aromatic-containing material and each R_0 is independently hydrogen, halo, or a C_1 - C_4 alkyl group. The alkyl group is usually methyl or ethyl. Examples of R_0 include hydrogen, chloro, bromo, fluoro, methyl, ethyl, n-propyl, isopropyl and n-butyl. Most commonly R_0 is hydrogen or methyl; hydrogen is preferred. A subclass of the divalent radical A_1 which is of particular usefulness is represented by the formula:

in which each R₁ is independently alkyl containing from 1 to about 4 carbon atoms, phenyl, or halo; the average value of each (a) is independently in the range of from 0 to 4; each Q is independently oxy, sulfonyl, alkanediyl having from 2 to about 4 carbon atoms, or alkylidene having from 1 to about 4 carbon atoms; and the average value of n is in the range of from 0 to about 3. Preferably Q is methylethylidene, viz., isopropylidene.

Preferably the value of n is zero, in which case A₁ is represented by the formula:

$$\begin{array}{c|c} (R_1)a & (R_1)a \\ \hline \end{array}$$

in which each R₁, each a, and Q are as discussed in respect of Formula II. Preferably the two free bonds are both in the ortho or para positions. The para positions are especially preferred.

The dihydroxy aromatic-containing compounds from which A_1 is derived may also be polyether-functional chain extended compounds. Examples of such compounds include alkaline oxide extended bisphenols. Typically the alkaline oxide employed is ethylene oxide, propylene oxide, or mixtures thereof. By way of exemplification, when para, para-bisphenols are chain extended with ethylene oxide, the bivalent radical A_1 may often be represented by the formula:

where each R_1 , each a, and Q are as discussed in respect of Formula II, and the average values of j and k are each independently in the range of from about 1 to about 4.

A preferred aromatic-containing bis(allyl carbonate)-functional monomer is represented by the formula:

and is commonly known as bisphenol A bis(allyl carbonate).

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A wide variety of compounds may be used as the polyethylenic functional monomer containing two or three ethylenically unsaturated groups. A preferred polyethylenic functional compound containing two or three ethylenically unsaturated groups may be generally described as the acrylic acid esters and the methacrylic acid

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esters of aliphatic polyhydric alcohols, such as, for example, the di- and triacrylates and the di- and trimethacrylates of ethylene glycol, triethylene glycol, tetraethylene glycol, tetraethylene glycol, glycerol, diethyleneglycol, butyleneglycol, propyleneglycol, pentanediol, hexanediol, trimethylolpropane, and tripropyleneglycol. Examples of specific suitable polyethylenic - functional monomers containing two or three ethylenically unsaturated groups include trimethylolpropanetriacrylate (TMPTA), tetraethylene glycol diacrylate (TTEGDA), tripropylene glycol diacrylate (TRPGDA), 1,6 hexanedioldimethacrylate (HDDMA), and hexanedioldiacrylate (HDDA).

In general, a photoinitiator for initiating the polymerization of the lens forming composition preferably exhibits an absorption spectrum over the 300-400 nm range. High absorptivity of a photoinitiator in this range, however, is not desirable, especially when casting a thick lens. The following are examples of illustrative photoinitiator compounds: methyl benzoylformate, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 1-hydroxycyclohexyl phenyl ketone, 2,2-di-sec- butoxyacetophenone, 2,2-dimethoxy-2-phenyl-acetophenone, 2,2-dimethoxy-2-phenyl-acetophenone, benzoin methyl ether, benzoin isobutyl ether, benzoin, benzil, benzyl disulfide, 2,4-dihydroxybenzophenone, benzylideneacetophenone, benzophenone and acetophenone. Preferred photoinitiator compounds are 1-hydroxycyclohexyl phenyl ketone (which is commercially available from Ciba-Geigy as Irgacure 184), methyl benzoylformate (which is commercially available from Polysciences, Inc.), or mixtures thereof.

Methyl benzoylformate is a generally preferred photoinitiator because it tends to provide a slower rate of polymerization. The slower rate of polymerization tends to prevent excessive heat buildup (and resultant cracking of the lens) during polymerization. In addition, it is relatively easy to mix liquid methyl benzoylformate (which is liquid at ambient temperatures) with many acrylates, diacrylates, and allyl carbonate compounds to form a lens forming composition. The lenses produced with the methyl

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benzoylformate photoinitiator tend to exhibit more favorable stress patterns and uniformity.

A strongly absorbing photoinitiator will absorb most of the incident light in the first millimeter of lens thickness, causing rapid polymerization in that region. The remaining light will produce a much lower rate of polymerization below this depth and will result in a lens that has visible distortions. An ideal photoinitiator will exhibit high activity, but will have a lower extinction coefficient in the useful range. A lower extinction coefficient of photoinitiators at longer wavelengths tends to allow the activating light to penetrate deeper into the reaction system. This deeper penetration of the activating light allows photoinitiator radicals to form uniformly throughout the sample and provide excellent overall cure. Since the sample may be irradiated from both top and bottom, a system in which appreciable activating light reaches the center of the thickest portion of the lens is preferred. The photoinitiator solubility and compatibility with the monomer system is also an important requirement.

An additional consideration is the effect of the photoinitiator fragments in the finished polymer. Some photoinitiators generate fragments that impart a yellow color to the finished lens. Although such lenses actually absorb very little visible light, they may be cosmetically undesirable.

Photoinitiators are often very system specific so that photoinitiators that are efficient in one system may function poorly in another. In addition, the initiator concentration, to a large extent, may be dependent on the incident light intensity and the monomer composition. The identity of the initiator and its concentration may be important for any particular formulation. A concentration of initiator that is too high may lead to cracking and yellowing of the lens. Concentrations of initiator that are too low may lead to incomplete polymerization and a soft material.

Dyes and/or pigments are optional materials that may be present when high transmission of light is not necessary.

The listing of optional ingredients discussed above is by no means exhaustive.

These and other ingredients may be employed in their customary amounts for their customary purposes so long as they do not seriously interfere with good polymer formulating practice.

1. Activating Light Curable Lens Forming Compositions

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According to a preferred embodiment, a lens forming composition that may be cured with activating light includes an aromatic-containing bis(allyl carbonate) functional monomer, preferably bisphenol A bis(allyl carbonate), admixed with one or more faster reacting polyethylenic functional monomers containing two acrylate or methacrylate groups such as 1,6 hexanediol dimethacrylate (HDDMA), 1,6 hexanediol diacrylate (HDDA), tetraethylene glycol diacrylate (TTEGDA), and tripropylene glycol diacrylate (TRPGDA) and optionally a polyethylenic functional monomer containing three acrylate groups such as trimethylolpropane triacrylate (TMPTA). Generally, compounds containing acrylate groups polymerize much faster than those containing allyl groups.

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According to one embodiment, the liquid lens forming composition includes bisphenol A bis(allyl-carbonate) in place of DEG-BAC. The bisphenol A bis(allyl-carbonate) monomer has a higher refractive index than DEG-BAC making it more suitable for the production of thinner lenses, which may be important with relatively thick positive or negative lenses. The bisphenol A bis(allyl-carbonate) monomer is commercially available from PPG Industries under the trade name HIRI I or CR-73. Lenses made from this product sometimes have a very slight, barely detectable, degree of yellowing. A small amount of a blue dye consisting of 9, 10-anthracenedione, 1-hydroxy-4-[(4-methylphenyl)amino] available as Thermoplast Blue 684 from BASF

Wyandotte Corp. is preferably added to the composition to counteract the yellowing. In addition, the yellowing tends to disappear if the lens is subjected to the above-described post-cure heat treatment. Moreover, if not post-cured the yellowing tends to disappear at ambient temperature after approximately 2 months.

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TTEGDA, available from Sartomer and Radcure, is a diacrylate monomer that, preferably, is included in the composition because it is a fast polymerizing monomer that reduces yellowing and yields a very clear product. If too much TTEGDA is included in the more preferred composition, i.e., greater than about 25% by weight, however, the finished lens may be prone to cracking and may be too flexible as this material softens at temperatures above 40 °C. If TTEGDA is excluded altogether, the finished lens may be too brittle.

HDDMA, available from Sartomer, is a dimethacrylate monomer that has a very stiff backbone between the two methacrylate groups. HDDMA, preferably, is included in the composition because it yields a stiffer polymer and increases the hardness and strength of the finished lens. This material is quite compatible with the bisphenol A bis(allyl carbonate) monomer. HDDMA contributes to high temperature stiffness, polymer clarity and speed of polymerization.

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TRPGDA, available from Sartomer and Radcure, is a diacrylate monomer that, preferably, is included in the composition because it provides good strength and hardness without adding brittleness to the finished lens. This material is also stiffer than TTEGDA.

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TMPTA, available from Sartomer and Radcure, is a triacrylate monomer that, preferably, is included in the composition because it provides more crosslinking in the finished lens than the diffunctional monomers. TMPTA has a shorter backbone than TTEGDA and increases the high temperature stiffness and hardness of the finished lens.

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Moreover, this material contributes to the prevention of optical distortions in the finished lens. TMPTA also contributes to high shrinkage during polymerization. The inclusion of too much of this material in the more preferred composition may make the finished lens too brittle.

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Certain of the monomers that are preferably utilized, such as TTEGDA, TRPGDA and TMPTA, include impurities and have a yellow color in certain of their commercially available forms. The yellow color of these monomers is preferably reduced or removed by passing them through a column of alumina (basic) which includes aluminum oxide powder - basic. After passage through the alumina column differences between monomers obtained from different sources may be substantially eliminated. It is preferred, however, that the monomers be obtained from a source which provides the monomers with the least amount of impurities contained therein. The composition is preferably filtered prior to polymerization thereof to remove suspended particles.

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2. Lens Forming Compositions Including Ultraviolet/Visible Light Absorbing Materials

Materials that absorb various degrees of ultraviolet/visible light may be used in an eyeglass lens to inhibit ultraviolet/visible light from being transmitted through the eyeglass lens. The phrase "ultraviolet/visible light" is taken to mean light having a wavelength in the ultraviolet light range or both the ultraviolet and visible light ranges. The phrase "ultraviolet/visible light absorbing compounds" refers to compounds which absorb ultraviolet/visible light. An eyeglass lens that includes ultraviolet/visible light absorbing compounds advantageously inhibits ultraviolet/visible light from being transmitted to the eye of a user wearing the lens. Thus, eyeglass lenses containing ultraviolet/visible light absorbing compounds may function to protect the eyes of a person from damaging ultraviolet/visible light. Photochromic pigments are one type of ultraviolet/visible light absorbing compounds. Photochromic inorganic lenses which contain silver halide particles or cuprous halide particles suspended throughout the body

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of the lens are well known and have been commercially available for decades. Such inorganic lenses, however, suffer the disadvantage of being relatively heavy and less comfortable to the wearer when compared to organic lenses. Consequently, the majority of the eyeglass lenses produced today are typically formed from organic materials rather than inorganic materials. Accordingly, photochromic plastic eyeglass lenses have been the subject of considerable attention in recent years.

Efforts to provide a plastic eyeglass lens which demonstrates photochromic performance have primarily centered around permeating and/or covering the surface(s) of an already formed lens with photochromic pigments. This general technique may be accomplished by a number of specific methods. For example, (a) the lens may be soaked in a heated bath which contains photochromic pigments, (b) photochromic pigments may be transferred into the surface of a plastic lens via a solvent assisted transfer process, or (c) a coating containing photochromic pigments may be applied to the surface of a lens. A problem with such methods may be that the lens often might not absorb enough of the photochromic pigments at low temperatures, resulting in an eyeglass lens which does not exhibit acceptable photochromic performance. Unfortunately, increasing the temperature used during absorption of the photochromic pigments may not be a solution to this problem since at high temperatures degradation of the polymer contained within the lens may occur.

Attempts have also been made to incorporate photochromic pigments into the liquid monomer from which plastic lenses are thermally polymerized. See U.S. Patent No. 4,913,544 to Rickwood et al., wherein it is disclosed that triethyleneglycol dimethacrylate monomer was combined with 0.2% by weight of various spiro-oxazine compounds and 0.1% benzoyl peroxide and subsequently thermally polymerized to form non-prescription eyeglass lenses. Generally, efforts to incorporate photochromic pigments into the liquid monomer from which the lenses are polymerized have been unsuccessful. It is believed that the organic peroxide catalysts utilized to initiate the

thermal polymerization reaction tend to damage the photochromic pigments, impairing their photochromic response.

Curing of an eyeglass lens using activating light to initiate the polymerization of a lens forming composition generally requires that the composition exhibit a high degree of activating light transmissibility so that the activating radiation may penetrate to the deeper regions of the lens cavity. Otherwise the resulting cast lens may possess optical aberrations and distortions. The cast lens may also contain layers of cured material in the regions closest to the transparent mold faces, sandwiching inner layers which are either incompletely cured, gelled, barely gelled, or even liquid. Often, when even small amounts of ultraviolet/visible light absorbing compounds of the types well known in the art are added to a normally light curable lens forming composition, substantially the entire amount of lens forming composition contained within the lens cavity may remain liquid in the presence of activating light.

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Photochromic pigments which have utility for photochromic eyeglass lenses absorb ultraviolet light strongly and change from an unactivated state to an activated state when exposed to ultraviolet light. The presence of photochromic pigments, as well as other ultraviolet/visible light absorbing compounds within a lens forming composition, generally does not permit enough activating radiation to penetrate into the depths of the lens cavity sufficient to cause photoinitiators to break down and initiate polymerization of the lens forming composition. Thus, it may be difficult to cure a lens forming composition containing ultraviolet/visible light absorbing compounds using activating light (e.g., if the activating light has a wavelength in the ultraviolet or visible region). It is therefore desirable to provide a method for using activating light to initiate polymerization of an eyeglass lens forming monomer which contains ultraviolet/visible light absorbing compounds, in spite of the high activating light absorption characteristics of the ultraviolet/visible light absorbing compounds. Examples of such ultraviolet/visible

light absorbing compounds other than photochromic pigments are fixed dyes and colorless additives.

In an embodiment, an ophthalmic eyeglass lens may be made from a lens forming composition comprising a monomer, an ultraviolet/visible light absorbing compound, a photoinitiator, and a co-initiator. Herein, an "ophthalmic eyeglass lens" is taken to mean any plastic eyeglass lens, including a prescription lens, a non-prescription lens, a progressive lens, a sunglass lens, and a bifocal lens. The lens forming composition, in liquid form, is preferably placed in a mold cavity defined by a first mold member and a second mold member. It is believed that activating light which is directed toward the mold members to activate the photoinitiator causes the photoinitiator to form a polymer chain radical. The polymer chain radical preferably reacts with the co-initiator more readily than with the monomer. The co-initiator may react with a fragment or an active species of either the photoinitiator or the polymer chain radical to produce a monomer initiating species in the regions of the lens cavity where the level of activating light may be either relatively low or not present.

Preferably, the monomers selected as components of the lens forming composition are capable of dissolving the ultraviolet/visible light absorbing compounds added to them. Herein, "dissolving" is taken to mean being substantially homogeneously mixed with. For example, monomers may be selected from a group including polyether (allyl carbonate) monomers, multi-functional acrylate monomers, and multi-functional methacrylic monomers for use in an ultraviolet/visible light absorbing lens forming composition.

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In an embodiment, the following mixture of monomers, hereinafter referred to as PRO-629, may be blended together before addition of other components required to make the lens forming composition. This blend of monomers is preferably used as the basis for

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a lens forming composition to which ultraviolet/visible light absorbing compounds are added.

32% Tripropyleneglycol diacrylate (SR-306)
21% Tetraethyleneglycol diacrylate (SR-268)
20% Trimethylolpropane triacrylate (SR-351)
17% Bisphenol A bis allyl carbonate (HiRi)
10% Hexanediol dimethacrylate (SR-239)

The acrylic and methacrylic monomers listed above are commercially available from Sartomer Company in Exton, Pennsylvania. The bisphenol A bis allyl carbonate is commercially available from PPG in Pittsburgh, Pennsylvania. The hexanediol dimethacrylate is hereinafter referred to as HDDMA.

A polymerization inhibitor may be added to the monomer mixture at relatively low levels to inhibit polymerization of the monomer at inappropriate times (e.g., during storage). Preferably about 0 to 50 ppm of monomethylether hydroquinone (MEHQ) are added to the monomer mixture. It is also preferred that the acidity of the monomer mixture be as low as possible. Preferably less than about 100 ppm residual acrylic acid exists in the mixture. It is also preferred that the water content of the monomer mixture be relatively low, preferably less than about 0.15 %.

Photoinitiators include: 1-hydroxycyclohexylphenyl ketone commercially available from Ciba Additives under the trade name of Irgacure 184; mixtures of bis(2,6-dimethoxybenzoyl) (2,4,4-trimethyl phenyl) phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one commercially available from Ciba Additives under the trade name of Irgacure 1700; mixtures of bis(2,6-dimethoxybenzoyl) (2,4,4 trimethyl phenyl) phosphine oxide and 1-hydroxycyclohexylphenyl ketone commercially available from Ciba Additives under the trade names of Irgacure 1800 and Irgacure 1850; 2,2-

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dimethoxy-2-phenyl acetophenone commercially available from Ciba Additives under the trade name of Irgacure 651; 2-hydroxy-2-methyl-1-phenyl-propan-1-one commercially available from Ciba Additives under the trade names of Darocur 1173; mixtures of 2,4,6trimethylbenzoyl-diphenylphoshine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1one commercially available from Ciba Additives under the trade name of Darocur 4265; 2,2-diethoxyacetophenone (DEAP) commercially available from First Chemical Corporation of Pascagoula, Mississippi, benzil dimethyl ketal commercially available from Sartomer Company under the trade name of KB-1; an alpha hydroxy ketone initiator commercially available from Sartomer company under the trade name of Esacure KIP100F; 2-methyl thioxanthone (MTX), 2-chloro-thioxanthone (CTX), thioxanthone (TX), and xanthone, all commercially available from Aldrich Chemical; 2-isopropylthioxanthone (ITX) commercially available from Aceto Chemical in Flushing, New York; mixtures of triaryl sulfonium hexafluoroantimonate and propylene carbonate commercially available from Sartomer Company under the trade names of SarCat CD 1010, SarCat 1011, and SarCat KI85; diaryliodinium hexafluoroantimonate commercially available from Sartomer Company under the trade name of SarCat CD-1012; mixtures of benzophenone and 1-hydroxycyclohexylphenyl ketone commercially available from Ciba Additives under the trade name of Irgacure 500; 2-benzyl-2-N,N-dimethylamino-1-(4morpholinophenyl)-1-butanone commercially available from Ciba Additives under the trade name of Irgacure 369; 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1one commercially available from Ciba Additives under the trade name of Irgacure 907; bis(n5-2,4-cyclopentadien-1-yl)-bis-[2,6-difluoro-3-(1H-pyrrol-1-yl) phenyl] titanium commercially available from Ciba Additives under the trade name of Irgacure 784 DC; mixtures of 2,4,6-trimethyl-benzophenone and 4-methyl-benzophenone commercially available from Sartomer Company under the trade name of EsaCure TZT; and benzoyl peroxide and methyl benzoyl formate both available from Aldrich Chemical in Milwaukee, Wisconsin.

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A preferred photoinitiator is bis(2,6-dimethoxybenzoyl) (2,4,4 trimethyl phenyl) phosphine oxide, commercially available from Ciba Additives in Tarrytown, New York under the trade name of CGI-819. The amount of CGI-819 present in a lens forming composition containing photochromic compounds preferably ranges from about 30 ppm by weight to about 2000 ppm by weight.

Co-initiators include reactive amine co-initiators commercially available from Sartomer Company under the trade names of CN-381, CN-383, CN-384, and CN-386, where these co-initiators are monoacrylic amines, diacrylic amines, or mixtures thereof. Other co-initiators include N-methyldiethanolamine (NMDEA), triethanolamine (TEA), ethyl-4-dimethylaminobenzoate (E-4-DMAB), ethyl-2-dimethylaminobenzoate (E-2-DMAB), all commercially available from Aldrich Chemicals. Co-initiators which may also be used include n-butoxyethyl-4-dimethylamino benzoate, p-dimethyl amino benzaldehyde. Other co-initiators include N, N-dimethyl-p-toluidine, octyl-p-(dimethylamino) benzoate commercially available from The First Chemical Group of Pascagoula, Mississippi.

Preferably, the co-initiator is N-methyldiethanolamine (NMDEA) commercially available from Aldrich Chemical in Milwaukee, Wisconsin, CN-384 commercially available from Sartomer Company, or CN-386 also commercially available from Sartomer Company. The quantity of NMDEA present in a lens forming composition containing photochromic pigments is preferably between about 1 ppm by weight and 7% by weight and more preferably between about 0.3% and 2% by weight. Further, certain fixed pigments which may be added to the lens forming composition to create a background color within the lens (i.e., to tint the lens), may also function as co-initiators. Examples of such fixed pigments include Thermoplast Blue P, Oil Soluble Blue II, Thermoplast Red 454, Thermoplast Yellow 104, Zapon Brown 286, Zapon Brown 287, all commercially available from BASF Corporation in Holland, Michigan.

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Ultraviolet/visible light absorbing compounds which may be added to a normally ultraviolet/visible light transmissible lens forming composition include 2-(2H benzotriazole-2-yl)-4-(1,1,3,3 tetramethylbutyl)phenol and 2-hydroxy-4-methoxybenzophenone, both commercially available from Aldrich Chemical as well as mixtures of 2-[4-((2-hydroxy-3-dodecyloxypropyl)-oxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine and 2-[4-((2-hydroxy-3-tridecyloxypropyl)-oxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl-1,3,5-triazine commercially available from Ciba Additives under the trade name of Tinuvin 400, mixtures of poly (oxy-1,2-ethanediyl), α-(3-(3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl)-1-oxopropyl)-ω-(3-(3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl)-1-oxopropyl)-ω-(3-(3-(2H-benzotriazol-2-yl)-5-1,1-dimethylethyl)-4-hydroxyphenyl)-1-oxopropoxy) commercially available from Ciba Additives under the trade name of Tinuvin 1130. Other ultraviolet/visible light absorbers may include Tinuvin 328, Tinuvin 900, 2-(2 hydroxy-5-methyl-phenyl) benzotriazole, ethyl-2-cyano 3,3-diphenyl acrylate, and phenyl salicylate.

While any number of families of photochromic pigments may be incorporated into the blend of monomers, either individually or in combination, spiropyrans, spiropyrans, spiropyridobenzoxazines, spirobenzoxazines, napthopyrans, benzopyrans, spirooxazines, spironapthopyrans, indolinospironapthoxazines, indolinospironapthopyrans, diarylnapthopyrans, and organometallic materials are of particular interest. A phenylmercury compound available from Marks Polarized Corporation in Hauppauge, New York under the trade name of A241 may be an appropriate organometallic material. The quantity of photochromic pigments present in the lens forming composition is preferably sufficient to provide observable photochromic effect. The amount of photochromic pigments present in the lens forming composition may widely range from about 1 ppm by weight to 5% by weight. In preferred compositions, the photochromic pigments are present in ranges from about 30 ppm to 2000 ppm. In the more preferred compositions, the photochromic pigments are present in

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ranges from about 150 ppm to 1000 ppm. The concentration may be adjusted depending upon the thickness of the lens being produced to obtain optimal visible light absorption characteristics.

In an embodiment, hindered amine light stabilizers may be added to the lens forming composition. It is believed that these materials act to reduce the rate of degradation of the cured polymer caused by exposure to ultraviolet light by deactivating harmful polymer radicals. These compounds may be effective in terminating oxygen and carbon free radicals, and thus interfering with the different stages of auto-oxidation and photo-degradation. A useful hindered amine light stabilizer is bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate commercially available from Ciba Additives under the trade name of Tinuvin 292. Hindered phenolic anti-oxidants and thermal stabilizers may also be added to a lens forming composition. The hindered phenolic compounds hereof include thiodiethylene bis(3,5,-di-tert-butyl-4-hydroxy)hydroxycinnamate commercially available from Ciba Additives under the trade name of Irganox 1035 and octadecyl-3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene-propanoate commercially available from Ciba Additives under the trade name of Irganox 1076.

Preferably, more than one monomer and more than one initiator are used in a lens forming composition to ensure that the initial polymerization of the lens forming composition with activating light does not occur over too short a period of time. The use of such a lens forming composition may allow greater control over the gel formation, resulting in better control of the optical quality of the lens. Further, greater control over the rate of exothermic heat generation may be achieved. Thus, cracking of the lens and premature release of the lens from the mold which are typically caused by the release of heat may be prevented. An example of a poor initiator system was observed when CGI-819 was used alone as a photoinitiator in combination with the PRO-629 monomer blend to which ultraviolet/visible light absorbing compounds had been added. When such an initiator system was used, a fast rate of reaction occurred near the surface of the lens

cavity while a very slow rate of reaction occurred in the deeper regions of the cavity. The resultant lens exhibited unwanted waves and distortions.

In another example, a small amount of a co-initiator, i.e., NMDEA was added to the above lens forming composition. During the curing process, two separate waves of heat were generated when the composition was irradiated continuously with activating light at about 600 microwatts/cm². One possible explanation for this phenomena is that the first wave resulted from reaction of the NMDEA and the second wave resulted from the reaction of the unconsumed portion of the CGI-819. Another possible explanation is that the rate of reaction was faster in the top portion than in the bottom portion of the lens forming composition since activating light was separately directed toward both the bottom and the top mold members. A third wave of heat generation may also occur if the rate of reaction at the middle portion of the lens forming composition is different from the rates at the bottom and top portions. Unfortunately, the resulting lens possessed waves and distortions. It is postulated, however, that as the amounts of both CGI-819 and NMDEA are increased, the two waves of exothermic heat will move closer together in time, causing the optical quality of the lens to improve, the hardness of the lens to increase, and the rate of heat generation to be slow enough to prevent cracking and premature release of the lens from the mold.

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It is anticipated that the optimal amount of initiators may be achieved when the total amount of both initiators are minimized subject to the constraint of complete polymerization and production of a rigid, aberration free lens. The relative proportions of the photoinitiator to the co-initiator may be optimized by experimentation. For example, an ultraviolet/visible light absorptive lens forming composition that includes a photoinitiator with no co-initiator may be cured. If waves and distortions are observed in the resulting lens, a co-initiator may then be added to the lens forming composition by increasing amounts until a lens having the best optical properties is formed. It is anticipated that excess co-initiator in the lens forming composition should be avoided to

inhibit problems of too rapid polymerization, yellowing of the lens, and migration of residual, unreacted co-initiator to the surface of the finished lens.

The following charts may be used as a guide in the selection of an appropriate photoinitiator/co-initiator system for various ultraviolet/visible light absorbing lens forming compositions.

Photoinitiator Guide

				Lens Forming Composition Type		
				UV Absorptive	UV Absorptive	UV Absorptive
Photoinitiator	Yellowness	Odor	Shelf Life	Photochromic	Fixed Pigments	Colorless
CGI 819	Moderate	Low	Good	Good	Good	Good
Irgacure 184	Low	Low	Good	Good	Good	Good
Irgacure 651	High	Low	Poor	Less Preferred	Good	Less Preferred
Irgacure 1700	High	Low	Fair	Good	Good	Less Preferred
Irgacure 1800	Moderate	Low	Good	Good	Good	Less Preferred
Irgacure 1850	Moderate	Low	Good	Good	Good	Good
Darocur 1173	High	Low	Good	Good	Good	Less Preferred
Darocur 4265	High	Moderate	Fair	Good	Good	Less Preferred
DEAP	High	Strong	Poor	Less Preferred	Less Preferred	Less Preferred
KB-1	High	Strong	Poor	Less Preferred	Less Preferred	Less Preferred
EsaCure KIP100F	High	Strong	Poor	Less Preferred	Less Preferred	Less Preferred
Irgacure 369	High	Moderate	Poor	Less Preferred	Good	Less Preferred
Irgacure 500	High	Strong	Poor	Less Preferred	Less Preferred	Less Preferred
Irgacure 784 DC	Hìgh	Low	Poor	Less Preferred	Less Preferred	Less Preferred
Irgacure 907	High	Strong	Poor	Less Preferred	Less Preferred	Less Preferred
Benzoyl peroxide	Moderate	Low	Poor	Less Preferred	Less Preferred	Less Preferred
Methyl benzoyl formate	Moderate	Low	Fair	Less Preferred	Less Preferred	Less Preferred
EsaCure TZT	High	Low	Poor	Less Preferred	Less Preferred	Less Preferred
ITX	High	Low	Poor	Less Preferred	Good	Good
MTX	High	Low	Poor	Less Preferred	Good	Good
CTX	High	Low	Poor	Less Preferred	Less Preferred	Less Preferred
TX	High	Low	Poor	Less Preferred	Less Preferred	Less Preferred
Xanthone	High	Low	Poor	Less Preferred	Less Preferred	Less Preferred
CD-1010	Low	Low	Poor	Good	Less Preferred	Less Preferred
CD-1011	Low	Low	Poor	Good	Less Preferred	Less Preferred
CD1012	Low	Low	Poor	Good	Good	Good

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Co-initiator Guide

	Lens Forming Composition Type				
Co-initiator	UV Absorptive Photochromic	UV Absorptive Fixed Pigments	UV Absorptive Colorless		
CN-383		Good			
CN-384	Good	Good	Good		
CN-386	Good	Good	Good		
NMDEA	Good	Good	Good		
N,NMDEA	Less Preferred	Less Preferred			
TEA	Less Preferred	Less Preferred			
E-4-DMAB	Good	Less Preferred	Less Preferred		
E-2-DMAB		Less Preferred	Less Preferred		

As mentioned above, exothermic reactions occur during the curing process of the lens forming composition. The thicker portions of the lens forming composition may generate more heat than the thinner portions of the composition as a result of the exothermic reactions taking place. It is believed that the speed of reaction in the thicker sections is slower than in the thinner sections. Thus, in a positive lens a "donut effect" may occur in which the relatively thin outer portion of the lens forming composition reaches its fully cured state before the relatively thick inner portion of the lens forming composition. Conversely, in a negative lens the relatively thin inner portion of the lens forming composition may reach its fully cured state before the relatively thick outer portion of the lens forming composition.

An eyeglass lens formed using the above described lens forming composition may be applicable for use as a prescription lens or for a non-prescription lens. Particularly, such a lens may be used in sunglasses. Advantageously, photochromic sunglass lenses would remain light enough in color to allow a user to see through them clearly while at the same time prohibiting ultraviolet light from passing through the lenses. In one

embodiment, a background dye may be added to the photochromic lens to make the lens appear to be a dark shade of color at all times like typical sunglasses.

3. Variable Color Photochromic Lens Forming Compositions

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Photochromic compounds tend to absorb certain wavelengths of light strongly and change from a colorless state to a colored state. The "colorless state" of a photochromic compound is defined as the state in which the compound exhibits no color or only a slight amount of color. The "colored state" of a photochromic compound is defined as the state in which the photochromic compound exhibits a visible light color significantly stronger than the colorless state. A "photochromic activating light source" is defined as any light source that produces light having a wavelength which causes a photochromic compound to change from a colorless state to a colored state. "Photochromic activating light" is defined as light having a wavelength capable of causing a photochromic compound to change from a colorless state to a colored state. Photochromic activating light typically includes light having a wavelength from between about 200 nm to about 500 nm. A photochromic activating light source may also produce other wavelengths of light, besides photochromic activating light.

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A photochromic compound which is transparent and normally colorless will, upon exposure to a photochromic activating light source (e.g., ultraviolet light), become colored and, therefore, less visible light transmissive. When removed from the photochromic activating light source, the photochromic substance tends to revert back to its colorless state. This may be represented by the following equation:

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The colorless form is believed to be in equilibrium with the colored form. The equilibrium between the colorless form and the colored form may be controlled by the presence of photochromic activating light (represented by hv). If a photochromic compound is exposed to a photochromic activating light source, the equilibrium tends to shift toward the colored form of the photochromic compound. When the photochromic activating light source is removed, or reduced, or if the photochromic compound is heated, the equilibrium tends to shift back toward the colorless form of the photochromic compound. Photochromic compounds of this type may be particularly useful in eyeglass lenses. In the absence of photochromic activating light (e.g., when indoors) the glasses tend to remain colorless and light transmissive. When exposed to a photochromic activating light source (e.g., sunlight) the photochromic compounds become activated and colored, lowering the light transmittance of the lens. The term "activated color" is defined as the color which an eyeglass attains when photochromic compounds, which are included in the eyeglass lens, become activated and colored when exposed to a photochromic activating light source. In this manner, photochromic compounds may allow a single lens to be used as both an indoor lens and an outdoor lens.

When incorporated into transparent plastic lenses and activated by exposure to a photochromic activating light source, photochromic compounds tend to exhibit variety of colors (e.g., red, orange, yellow, green, blue, indigo, purple, violet, gray, and brown), causing the lens that the photochromic compounds are disposed within to exhibit the color of the photochromic compound. Thus, the activated color of a photochromic eyeglass lens may be controlled by the particular photochromic compounds dispersed within the eyeglass lens.

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It is known that the activated color of a photochromic eyeglass lens may take on more neutral colors, such as brown or gray, by forming the eyeglass lens with two or more photochromic compounds present. U.S. Patent No. 4,968,454 to Crano et. al., describes a composition which includes two photochromic compounds used to form

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photochromic compounds are present, the equilibrium between the colored and the colorless forms may be represented by the following equations:

Where PC¹ Colorless represents the colorless form of the first photochromic compound; 5 PC² Colorless represents the colorless form of the second photochromic compound; PC light represents the wavelengths of light which cause PC1 Colorless to shift its colored state (PC¹ Colored); PC light² represents the wavelengths of light which cause PC¹ Colorless to shift to its colored state (PC² Colored). As depicted in Fig. 37, the wavelength of light which may activate the photochromic compounds PC¹ and PC² may 10 differ depending on the chemical structure of the photochromic compounds. PC light¹, which activates the first photochromic compound PC¹, has a wavelength in the range between about λ^1 and λ^2 nm. PC light, which activates the second photochromic compound, has a wavelength in the range between about λ^3 and λ^4 nm. These wavelength ranges may differ (as depicted in Fig. 37) or may be substantially the same.

The addition of a light effector composition which absorbs photochromic activating light may cause a change in the activated color of the formed lens. The change in activated color may be dependent on the range of photochromic activating light absorbed by the light effector composition. The addition of light effector compositions may have different effects on the activated color of the lens, depending on the absorbance of the light effector composition. In one embodiment, the light effector composition may interfere with the photochromic activity of the first photochromic compound (PC1). As

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illustrated in the equations below, the presence of a light effector composition (Effector¹) may cause a shift in the equilibrium of PC¹ while having little or no effect on PC².

Such an effect may cause an increase or decrease in the concentration of PC¹ Colored produced when the lens is exposed to a photochromic activating light source. The equilibrium of the other photochromic compound PC² may not be significantly altered. Thus, the activated color of the lens may be significantly different than the activated color of a lens that does not include a light effector composition (Effector¹). In the above case, if the concentration of PC1 Colored is, for example, decreased, the activated color of the lens may become shifted toward the activated color of PC². For example, if the activated color of a lens which includes PC1 only is blue-green; with PC2 only is red; and with both PC1 and PC2 is gray; the activated color of the lens may become more red (e.g., shift from gray to green, yellow, orange or red) if the concentration of PC¹ Colored is decreased. It is theorized that such an effector may have an absorbance in a region of light similar to the PC Light¹ region. The effector may interfere with the absorption of photochromic activating light by PC¹ by competing with PC¹ for the light. PC² remains relatively unaffected by the light effector composition since its active photochromic activating light range differs significantly from the photochromic activating light range for PC¹. This is graphically illustrated in Fig. 37, where Effector¹ is depicted as having an absorption within the PC¹ Light¹ region. By competing with PC¹ for the photochromic activating light, Effector¹ may cause a decrease in the amount of PC¹ Colored being produced.

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In another embodiment, a light effector may interact with both photochromic compounds, altering the amount of PC¹ colored and PC² colored produced. The equation below depicts this case:

Such an effect may cause an increase or decrease in the concentration of both PC¹ Colored and PC² Colored produced when the lens is exposed to a photochromic activating light source. This change in the equilibrium may cause the activated color of the lens to be significantly different than the activated color of a lens that does not include a light effector composition. In the above case if the concentration of PC¹ Colored is, for example, decreased and the concentration of PC² Colored is, for example, increased, the activated color of the lens may become shifted toward the activated color of PC² colored. For example, if the activated color of a lens which includes PC¹ only is blue-green; with PC² only is red; and with both PC¹ and PC² is gray; the activated color of the lens may become more red in the presence of the light effector composition. The

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direction of the shift may depend on which photochromic compound is effected more by the presence of the light effector composition. It is theorized that the light effector composition (Effector²) may have an absorbance in a region that significantly overlaps the PC Light¹ and PC Light² regions. The light effector composition interferes with the absorption of photochromic activating light by both PC¹ and PC² by competing with the compounds for light having the appropriate activating wavelength. If the light effector interferes with the photochromic light absorption of PC¹ to a greater extent then PC² the color may shift toward PC². Alternatively, the activated color may shift toward PC¹ if the light effector absorption interferes with the absorption of photochromic light by PC² to a greater extent than PC¹. In Fig. 37, Effector² is depicted as having an absorption within both the PC¹ and PC² absorption region.

In another embodiment, a light effector composition may interfere with the photochromic activity of the second photochromic compound (PC²). As illustrated in the equations below, the presence of a light effector composition (Effector³) may cause a shift in the equilibrium of PC² while having little or no effect on PC¹.

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Such an effect may cause an increase or decrease in the concentration of PC2 Colored produced when the lens is exposed to a photochromic activating light source. The equilibrium of the other photochromic compound PC1 may not be significantly altered. In the above case, if the concentration of PC² Colored is, for example, decreased, the activated color of the lens may become shifted toward the activated color of PC1. For example, if the activated color of a lens which includes PC1 only is blue-green; with PC2 only is red; and with both PC1 and PC2 is gray; the activated color of the lens may become more blue (e.g., shift from gray to green, green-blue, or blue) if the concentration of PC1 Colored is decreased. It is theorized that such an effector may have an absorbance in a region of light similar to the PC Light² region. The effector may interfere with the absorption of photochromic activating light by PC² by competing with PC² for the light. PC1 remains relatively unaffected by the light effector composition since its active photochromic activating light range differs significantly from the photochromic activating light range for PC². This is graphically illustrated in Fig. 37, where Effector³ is depicted as having an absorption within the PC Light² region. By competing with PC² for the photochromic activating light, Effector³ may cause a decrease in the amount of PC² Colored being produced.

While the above examples relate to the use of two photochromic compounds, light effector compositions may be used to effect the activated color of a lens which includes more than two photochromic compounds. The color changes for these systems may be more varied than described above, due to the variety of ranges in which the photochromic compounds absorb the photochromic activating light. For example, if three photochromic compounds are present, with activated colors of red, blue and green, a variety of colors may be produced depending on the interaction of the light effector composition with the photochromic activating light. The light effector may absorb the photochromic activating light such that the concentration of the colored form of two of the three photochromic compounds is reduced. The formed lens would than exhibit a color which is closest to the activated color of the non-effected photochromic compound. In the above example, a

lens with an activated color of substantially blue, red, or green may be obtained by the addition of a light effector. Alternatively, the light effector compound may reduce the concentration of the colored form of only one of the photochromic compounds. In the above example, the activated color of the lens may become yellow (from red and green, with reduced amount of blue), green-blue (from green and blue, with reduced amount of red) or purple (from red and blue, with reduced amount of green). A full spectrum of activated colors may be produced by changing the composition of the light effector composition, without having to alter the ratio or chemical composition of the photochromic compounds.

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It should also be understood that the light effector composition may include one or more light effector compounds. The use of multiple light effector compounds may allow the activated color of the lens to be further altered.

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In another embodiment, a photochromic activating light dye may be added to the lens forming composition to alter the activated color of a lens. The dye preferably exhibits a dye color when exposed to visible light. The dye color, however, is not significantly altered in the presence or absence of photochromic activating light. When mixed with a lens forming composition which includes at least one photochromic compound the dye may alter the activated color of the lens, as well as the color of the lens in the absence of photochromic activating light.

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In one embodiment, the dye may interfere with the photochromic activity of a photochromic compound. The activated color of a lens formed without the dye would preferably change when the dye is added to the lens. The activated color of the lens may vary depending on the type of dye chosen. In one embodiment, the dye may interfere with the absorbance of photochromic activating light by the photochromic compound. This interference may lead to a reduced concentration of the colored form of the photochromic compound. The activated color of the lens may be a mixture of the dye

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color and the photochromic color. For example, if a dye is blue and the photochromic compound is red, the lens may take on a purple color (i.e., a combination of the two colors).

It should be understood that the activated color of the lens may be significantly different the an activated color of a lens in which the photochromic compound is unaffected by the dye. When the absorption of photochromic activating light by the photochromic compound is unaffected by the dye, the intensity of the colored form of the photochromic compound may not be reduced. Thus, the activated color of the lens is formed from a mixture of the dye color and the full intensity of the colored form of the photochromic compound. When the dye interferes with the photochromic activating light absorbance of the photochromic compound, the color of the lens is based on a combination of the dye and the reduced intensity of the colored form of the photochromic compound may cause the lens to have a color that is substantially different from the color produced when the unaffected colored form of the photochromic compound is mixed with the dye.

While described above for one photochromic compound, it should be understood that the dye may have an effect on mixtures of photochromic compounds such that a full spectrum of colors may be achieved. The selection of the appropriate dye based on the photochromic compounds present allows the color of the lenses to be altered without changing the ratio of the photochromic compounds.

In an embodiment, a lens forming composition includes at least two photochromic compounds. The photochromic compounds are preferably chosen to that have an activated color at opposite ends of the visible spectrum (e.g., blue and red). In one embodiment, the photochromic compounds may be Reversacol Berry Red (giving a red activated color) and Reversacol Sea Green (giving a blue-green color). The appropriate mixture of these two photochromic compounds gives the formed lens an activated color

of gray. The addition of effectors may cause the formed lens to have a wide variety of activated colors (e.g. red, orange, yellow, yellow green, green, aqua-green, blue, violet, purple, or brown). These changes in color may be accomplished without altering the ratio between the first and second photochromic compounds.

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A lens forming composition based on the PRO-629 mixture of monomers may be used to develop photochromic lenses (See the section entitled "Lens Forming Compositions Including Ultraviolet/Visible Light Absorbing Materials"). The remainder of the lens forming composition preferably includes photoinitiators, co-initiators, photochromic compounds. The amount of photochromic pigments present in the lens forming composition may widely range from about 1 ppm by weight to 5% by weight. In preferred compositions, the photochromic pigments are present in ranges from about 30 ppm to 2000 ppm. In the more preferred compositions, the photochromic pigments are present in ranges from about 150 ppm to 1000 ppm. The concentration may be adjusted depending upon the thickness of the lens being produced to obtain optimal visible light absorption characteristics.

To alter the color of the active lens formed from this base composition a light effector composition may be added to the base composition. The light effector composition preferably includes one or more light effectors. The light effector composition may be a pure composition of one or more light effectors. Alternatively, the light effectors may be diluted in a solution which has a composition similar to the base composition. The light effectors preferably include photochromic activating light absorbing compounds. More preferably, non-photochromic photochromic activating light absorbing compounds are added to alter the activated color of the formed lens. Examples of light effectors include polymerization inhibitors (e.g., MEHQ), photoinitiators, co-initiators, fixed pigments and dyes, and hindered amine light stabilizers. All of these classes of compounds are described in greater detail in the previous section. After the light effector composition has been added, the amount of light

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effectors present in the lens forming composition may widely range from about 1 ppm by weight to 5% by weight. In preferred compositions, the light effectors are present in ranges from about 30 ppm to 2000 ppm. In the more preferred compositions, the light effectors are present in ranges from about 150 ppm to 1000 ppm. The concentration may be adjusted depending upon the thickness of the lens being produced to obtain optimal visible light absorption characteristics.

An advantage of the described composition is that the activated color of a lens may be altered without altering the ratio and or composition of the photochromic compounds. By using a light effector composition, a single lens forming composition may be used as a base composition to which a light effector composition may be added in order to alter the activated color of the formed lens. The base composition may be supplied for use in the production of a variety of photochromic lenses. Along with the base composition, a light effector composition, which includes one or more light effector compounds, may be included with the base composition. The light effector composition may be added to the base composition to alter the activated color of the formed lenses. In this manner, a single stock photochromic lens forming composition may be used to create photochromic lenses having a variety of activated colors.

In another embodiment, the base composition and at least two light effector compositions may be package together as a kit. The addition of the first light effector composition may alter the activated color of the formed lenses to produce a first color. The addition of the second light effector composition may alter the activated color of the formed lenses to produce a second color. Additional light effectors compositions may also be included with the kit. The kit may allow a user to produce lens forming compositions which may be used to produce lens having a variety of activated colors by the addition of the appropriate light effector composition to the base composition.

4. Mid-Index Lens Forming Composition

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In an embodiment, an ophthalmic eyeglass lens may be made from a lens forming composition comprising a monomer composition and a photoinitiator composition.

The monomer composition preferably includes an aromatic containing polyethylenic polyether functional monomer. In an embodiment, the polyether employed is an ethylene oxide derived polyether, propylene oxide derived polyether, or mixtures thereof. Preferably, the polyether is an ethylene oxide derived polyether. The aromatic polyether polyethylenic functional monomer preferably has the general structure (V), depicted below where each R_2 is a polymerizable unsaturated group, m and n are independently 1 or 2, and the average values of j and k are each independently in the range of from about 1 to about 20. Common polymerizable unsaturated groups include vinyl, allyl, allyl carbonate, methacrylyl, acrylyl, methacrylate, and acrylate.

$$R_2$$
-[CH₂-(CH₂)_m-O]_i-A₁-[O-(CH₂)_n-CH₂]_k-R₂

 A_1 is the divalent radical derived from a dihydroxy aromatic-containing material. A subclass of the divalent radical A_1 which is of particular usefulness is represented by formula (II):

in which each R₁ is independently alkyl containing from 1 to about 4 carbon atoms, phenyl, or halo; the average value of each (a) is independently in the range of from 0 to 4; each Q is independently oxy, sulfonyl, alkanediyl having from 2 to about 4 carbon atoms,

or alkylidene having from 1 to about 4 carbon atoms; and the average value of n is in the range of from 0 to about 3. Preferably Q is methylethylidene, viz., isopropylidene.

Preferably the value of n is zero, in which case A₁ is represented by formula (III):

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$$\begin{array}{c|c} (R_1)a & (R_1)a \\ \hline \end{array}$$

in which each R₁, each a, and Q are as discussed with respect to Formula II. Preferably the two free bonds are both in the ortho or para positions. The para positions are especially preferred.

In an embodiment, when para, para-bisphenols are chain extended with ethylene oxide, the central portion of the aromatic containing polyethylenic polyether functional monomer may be represented by the formula:

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$$-\left(\text{CH}_{2}\text{CH}_{2}\text{C}\right)_{j}^{\text{(R_{1})a}} - \left(\text{OCH}_{2}\text{CH}_{2}\right)_{k}^{\text{(IV)}}$$

where each R₁, each a, and Q are as discussed with respect to Formula II, and the average values of j and k are each independently in the range of from about 1 to about 20.

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In another embodiment, the polyethylenic functional monomer is an aromatic polyether polyethylenic functional monomer containing at least one group selected from acrylyl or methacrylyl. Preferably the aromatic polyether polyethylenic functional

monomer containing at least one group selected from acrylate and methacrylate has the general structure (VI), depicted below where R_0 is hydrogen or methyl, where each R_1 , each a, and Q are as discussed with respect to Formula II, where the values of j and k are each independently in the range of from about 1 to about 20, and where R_2 is a polymerizable unsaturated group (e.g., vinyl, allyl, allyl carbonate, methacrylyl, acrylyl, methacrylate, or acrylate).

$$R_{2}-\left(H_{2}CH_{2}O\right)_{j} = Q - \left(OCH_{2}CH_{2}\right)_{k} - Q - \left(VI\right)_{k}$$

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In one embodiment, the aromatic containing polyether polyethylenic functional monomer is preferably an ethoxylated bisphenol A di(meth)acrylate. Ethoxylated bisphenol A di(meth)acrylates have the general structure depicted below where each R_0 is independently hydrogen or methyl, each R_1 , each a, and Q are as discussed with respect to Formula II, and the values of j and k are each independently in the range of from about 1 to about 20.

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Preferred ethoxylated bisphenol A dimethacrylates include ethoxylated 2 bisphenol A diacrylate (where j + k = 2, and R_0 is H), ethoxylated 2 bisphenol A

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dimethacrylate (where j+k=2, and R_0 is Me), ethoxylated 3 bisphenol A diacrylate (where j+k=3, and R_0 is H), ethoxylated 4 bisphenol A diacrylate (where j+k=4, and R_0 is H), ethoxylated 4 bisphenol A dimethacrylate (where j+k=4, and R_0 is Me), ethoxylated 6 bisphenol A dimethacrylate (where j+k=6, and R_0 is Me), ethoxylated 8 bisphenol A dimethacrylate (where j+k=8, and R_0 is Me), ethoxylated 10 bisphenol A diacrylate (where j+k=10, and R_0 is H), ethoxylated 10 bisphenol A dimethacrylate (where j+k=10, and R_0 is Me), ethoxylated 30 bisphenol A diacrylate (where j+k=30, and R_0 is H), ethoxylated 30 bisphenol A dimethacrylate (where j+k=30, and R_0 is H), ethoxylated 30 bisphenol A dimethacrylate (where j+k=30, and R_0 is Me). These compounds are commercially available from Sartomer Company under the trade names PRO-631, SR-348, SR-349, SR-601, CD-540, CD-541, CD-542, SR-602, SR-480, SR-9038, and SR-9036 respectively. Other ethoxylated bisphenol A dimethacrylates include ethoxylated 3 bisphenol A dimethacrylate (where j+k=30, and R_0 is Me), ethoxylated 6 bisphenol A diacrylate (where j+k=30, and R_0 is H), and ethoxylated 8 bisphenol A diacrylate (where j+k=30, and R_0 is H), In all of the above described compounds Q is $C(CH_3)_2$.

The monomer composition preferably may also include a polyethylenic functional monomer. Polyethylenic functional monomers are defined herein as organic molecules which include two or more polymerizable unsaturated groups. Common polymerizable unsaturated groups include vinyl, allyl, allyl carbonate, methacrylyl, acrylyl, methacrylate, and acrylate. Preferably, the polyethylenic functional monomers have the general formula (VII) or (VIII) depicted below, where each R_0 is independently hydrogen, halo, or a C_1 - C_4 alkyl group and where A_1 is as described above. It should be understood that while general structures (VII) and (VIII) are depicted as having only two polymerizable unsaturated groups, polyethylenic functional monomers having three (e.g., tri(meth)acrylates), four (e.g., tetra(meth)acrylates), five (e.g., penta(meth)acrylates), six (e.g., hexa(meth)acrylates) or more groups may be used.

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Preferred polyethylenic functional monomers which may be combined with an aromatic containing polyethylenic polyether functional monomer to form the monomer composition include, but are not limited to, ethoxylated 2 bisphenol A dimethacrylate, tris(2-hydroxyethyl)isocyanurate triacrylate, ethoxylated 10 bisphenol A dimethacrylate, ethoxylated 4 bisphenol A dimethacrylate, dipentaerythritol pentaacrylate, 1,6-hexanediol dimethacrylate, isobornyl acrylate, pentaerythritol triacrylate, ethoxylated 6 trimethylolpropane triacrylate, and bisphenol A bis allyl carbonate.

According to one embodiment, the liquid lens forming composition includes ethoxylated 4 bisphenol A dimethacrylate. Ethoxylated 4 bisphenol A dimethacrylate monomer, when cured to form an eyeglass lens, typically produces lenses that have a higher index of refraction than comparable lenses produced using DEG-BAC. Lenses formed from such a mid-index lens forming composition which includes ethoxylated 4 bisphenol A dimethacrylate may have an index of refraction of about 1.56 compared to the PRO-629 compositions (previously described) which tend to have an index of refraction of about 1.51. A lens made from a higher index of refraction polymer may be thinner than a lens made from a lower index of refraction polymer because the differences in the radii of curvature between the front and back surface of the lens do not have to be

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as great to produce a lens of a desired focal power. Lenses formed from a lens forming composition which includes ethoxylated 4 bisphenol A dimethacrylate may also be more rigid than lenses formed from PRO-629 based compositions.

The monomer composition may include additional monomers, which, when combined with ethoxylated 4 bisphenol A dimethacrylate, may modify the properties of the formed eyeglass lens and/or the lens forming composition. Tris(2hydroxyethyl)isocyanurate triacrylate, available from Sartomer under the trade name SR-368, is a triacrylate monomer that may be included in the composition to provide improved clarity, high temperature rigidity, and impact resistance properties to the finished lens. Ethoxylated 10 bisphenol A dimethacrylate, available from Sartomer under the trade name SR-480, is a diacrylate monomer that may be included in the composition to provide impact resistance properties to the finished lens. Ethoxylated 2 bisphenol A dimethacrylate, available from Sartomer under the trade name SR-348, is a diacrylate monomer that may be included in the composition to provide tintability properties to the finished lens. Dipentaerythritol pentaacrylate, available from Sartomer under the trade name SR-399, is a pentaacrylate monomer that may be included in the composition to provide abrasion resistance properties to the finished lens. 1,6-hexanediol dimethacrylate, available from Sartomer under the trade name SR-239, is a diacrylate monomer that may be included in the composition to reduce the viscosity of the lens forming composition. Isobornyl acrylate, available from Sartomer under the trade name SR-506, is an acrylate monomer that may be included in the composition to reduce the viscosity of the lens forming composition and enhance tinting characteristics. Bisphenol A bis allyl carbonate may be included in the composition to control the rate of reaction during cure and also improve the shelf life of the lens forming composition. Pentaerythritol triacrylate, available from Sartomer under the trade name SR-444, is a triacrylate monomer that may be included in the composition to promote better adhesion of the lens forming composition to the molds during curing. Ethoxylated 6 trimethylolpropane triacrylate, available from Sartomer under the trade name SR-454,

may also be added.

Photoinitiators which may be used in the lens forming composition have been described in previous sections. In one embodiment, the photoinitiator composition preferably includes phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide (IRG-819) which is commercially available from Ciba Additives under the trade name of Irgacure 819. The amount of Irgacure 819 present in a lens forming composition preferably ranges from about 30 ppm by weight to about 2000 ppm by weight. In another embodiment, the photoinitiator composition may include a mixture of photoinitiator. Preferably, a mixture of Irgacure 819 and 1-hydroxycyclohexylphenyl ketone, commercially available from Ciba Additives under the trade name of Irgacure 184 (IRG-184), is used. Preferably, the total amount of photoinitiators in the lens forming composition ranges from about 50 ppm to about 1000 ppm.

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In another embodiment, an ophthalmic eyeglass lens may be made from lens forming composition comprising a monomer composition, a photoinitiator composition, and a co-initiator composition. The lens forming composition, in liquid form, is preferably placed in a mold cavity defined by a first mold member and a second mold member. It is believed that activating light which is directed toward the mold members to activate the photoinitiator composition causes the photoinitiator to form a polymer chain radical. The co-initiator may react with a fragment or an active species of either the photoinitiator or the polymer chain radical to produce a monomer initiating species. The polymer chain radical and the monomer initiating species may react with the monomer to cause polymerization of the lens forming composition.

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The monomer composition preferably includes an aromatic containing polyethylenic polyether functional monomer having a structure as shown above.

Preferably, the polyethylenic functional monomer is an aromatic polyether polyethylenic functional monomer containing at least one group selected from acrylyl or methacrylyl.

More preferably, the polyethylenic functional monomer is an ethoxylated bisphenol A di(meth)acrylate. The monomer composition may include a mixture of polyethylenic functional monomers, as described above. The photoinitiators which may be present in the lens forming composition have been described above.

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The lens forming composition preferably includes a co-initiator composition. The co-initiator composition preferably includes amine co-initiators. Amines are defined herein as compounds of nitrogen formally derived from ammonia (NH₃) by replacement of the hydrogens of ammonia with organic substituents. Co-initiators include acrylyl amine co-initiators commercially available from Sartomer Company under the trade names of CN-381, CN-383, CN-384, and CN-386, where these co-initiators are monoacrylyl amines, diacrylyl amines, or mixtures thereof. Other co-initiators include ethanolamines. Examples of ethanolamines include but are not limited to N-methyldiethanolamine (NMDEA) and triethanolamine (TEA) both commercially available from Aldrich Chemicals. Aromatic amines (e.g., aniline derivatives) may also be used as co-initiators. Example of aromatic amines include, but are not limited to, ethyl-4-dimethylaminobenzoate (E-4-DMAB), ethyl-2-dimethylaminobenzoate (E-2-DMAB), n-butoxyethyl-4-dimethylaminobenzoate, p-dimethylaminobenzaldehyde, N, N-dimethyl-p-toluidine, and octyl-p-(dimethylamino)benzoate commercially available from Aldrich Chemicals or The First Chemical Group of Pascagoula, Mississippi.

Preferably, acrylated amines are included in the co-initiator composition. Acrylyl amines may have the general structures depicted in Fig. 39, where R₀ is hydrogen or methyl, n and m are 1 to 20, preferably 1-4, and R₁ and R₂ are independently alkyl containing from 1 to about 4 carbon atoms or phenyl. Monoacrylyl amines may include at least one acrylyl or methacrylyl group (see compounds (A) and (B) in FIG. 39). Diacrylyl amines may include two acrylyl, two methacrylyl, or a mixture of acrylyl or methacrylyl groups (see compounds (C) and (D) in FIG. 39). Acrylyl amines are commercially available from Sartomer Company under the trade names of CN-381, CN-

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383, CN-384, and CN-386, where these co-initiators are monoacrylyl amines, diacrylyl amines, or mixtures thereof. Other acrylyl amines include dimethylaminoethyl methacrylate and dimethylaminoethyl acrylate both commercially available from Aldrich. In one embodiment, the co-initiator composition preferably includes a mixture of CN-384 and CN-386. Preferably, the total amount of co-initiators in the lens forming composition ranges from about 50 ppm to about 7 % by weight.

An advantage to lens forming compositions which include a co-initiator is that less photoinitiator may be used to initiate curing of the lens forming composition.

Typically, plastic lenses are formed from a lens forming composition which includes a photoinitiator and a monomer. To improve the hardness of the formed lenses the concentration of photoinitiator may be increased. Increasing the concentration of photoinitiator, however, may cause increased yellowing of the formed lens, as has been described previously. To offset this increase in yellowing, a permanent dye may be added to the lens forming composition. As the amount of yellowing is increased the amount of dye added may also be increased. Increasing the concentration of the dye may cause the light transmissibility of the lens to decrease.

A lens forming composition that includes a co-initiator may be used to reduce the amount of photoinitiator used. To improve the hardness of the formed lenses a mixture of photoinitiator and co-initiator may be used to initiate curing of the monomer. The above-described co-initiators typically do not significantly contribute to the yellowing of the formed lens. By adding co-initiators to the lens forming composition, the amount of photoinitiator may be reduced. Reducing the amount of photoinitiator may decrease the amount of yellowing in the formed lens. This allows the amount of dyes added to the lens forming composition to be reduced and light transmissibility of the formed lens may be improved without sacrificing the rigidity of the lens.

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The lens forming composition may also include activating light absorbing compounds. These compounds may absorb at least a portion of the activating light which is directed toward the lens forming composition during curing. One example of activating light absorbing compounds are photochromic compounds. Photochromic compounds which may be added to the lens forming composition have been previously described. Preferably, the total amount of photochromic compounds in the lens forming composition ranges from about 1 ppm to about 1000 ppm. Examples of photochromic compounds which may be used in the lens forming composition include, but are not limited to Corn Yellow, Berry Red, Sea Green, Plum Red, Variacrol Yellow, Palatinate Purple, CH-94, Variacrol Blue D, Oxford Blue and CH-266. Preferably, a mixture of these compounds is used. Variacrol Yellow is a napthopyran material, commercially available from Great Lakes Chemical in West Lafayette, Indiana. Corn Yellow and Berry Red are napthopyrans and Sea Green, Plum Red and Palatinate Purple are spironaphthoxazine materials commercially available from Keystone Aniline Corporation in Chicago, Illinois. Variacrol Blue D and Oxford Blue are spironaphthoxazine materials, commercially available from Great Lakes Chemical in West Lafayette, Indiana. CH-94 and CH-266 are benzopyran materials, commercially available from Chroma Chemicals in Dayton, Ohio. The composition of a Photochromic Dye Mixture which may be added to the lens forming composition is described in Table 1.

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Photochromic Dye Mixture

Corn Yellow	22.3 %
Berry Red	19.7 %
Sea Green	14.8 %
Plum Red	14.0 %
Variacrol Yellow	9.7 %
Palatinate Purple	7.6 %
CH-94	4.0 %
Variacrol Blue D	3.7 %
Oxford Blue	2.6 %
CH-266	1.6 %

Table 1

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The lens forming composition may also other activating light absorbing compounds such as UV stabilizers, UV absorbers, and dyes. UV stabilizers, such as Tinuvin 770 may be added to reduce the rate of degradation of the formed lens caused by exposure to ultraviolet light. UV absorbers, such as 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3,-tetramethylbutyl)phenol, may be added to the composition to provide UV blocking characteristics to the formed lens. Small amounts of dyes, such as Thermoplast Blue 684 and Thermoplast Red from BASF may be added to the lens forming composition to counteract yellowing. These classes of compounds have been described in greater detail in previous sections.

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In an embodiment, a UV absorbing composition may be added to the lens forming composition. The UV absorbing composition preferably includes a photoinitiator and a UV absorber. Photoinitiators and UV absorbers have been described in greater detail in previous sections. Typically, the concentration of UV absorber in the lens forming

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composition required to achieve desirable UV blocking characteristics is in the range from about 0.1 to about 0.25 % by weight. For example, 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3,-tetramethylbutyl)phenol may be added to the lens forming composition as a UV absorber at a concentration of about 0.17 %.

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By mixing a photoinitiator with a UV absorbing compound the combined concentration of the photoinitiator and the UV absorber required to achieve the desired UV blocking characteristics in the formed lens may be lower than the concentration of UV absorber required if used alone. For example, 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3,tetramethylbutyl)phenol may be added to the lens forming composition as a UV absorber at a concentration of about 0.17 % to achieve the desired UV blocking characteristics for the formed lens. Alternatively, a UV absorbing composition may be formed by a combination of 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3,-tetramethylbutyl)phenol with the photoinitiator 2-isopropyl-thioxanthone (ITX), commercially available from Aceto Chemical in Flushing, New York. To achieve similar UV blocking characteristics in the formed lens, significantly less of the UV absorbing composition may be added to the lens forming composition, compared to the amount of UV absorber used by itself. For example, 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3,-tetramethylbutyl)phenol at a concentration of about 700 ppm, with respect to the lens forming composition, along with 150 ppm of the photoinitiator 2-isopropyl-thioxanthone (2-ITX) may be used to provide UV blocking characteristics. Thus, a significant reduction, (e.g., from 0.15 % down to less than about 1000 ppm), in the concentration of UV absorber may be achieved, without a reduction in the UV blocking ability of the subsequently formed lens. An advantage of lowering the amount of UV absorbing compounds present in the lens forming composition is that the solubility of the various components of the composition may be improved.

Tables 2-6 list some examples of mid-index lens forming compositions. The UV absorber is 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3,-tetramethylbutyl)phenol.

Ingredient	Formula 1	Formula 2	Formula 3	Formula 4	Formula 5	Formula 6
Irgacure 819	694.2 ppm	486 ppm	480 ppm	382 ppm	375 ppm	414 ppm
Irgacure 184						
CN 384	0.962 %	0.674%	0.757%	0.62%	0.61%	0.66%
CN386	0.962 %	0.674 %	0.757 %	0.62 %	0.61 %	0.66 %
SR-348	97.98 %	68.65 %	98.2 %	81.2 %	79.6 %	86.4 %
SR-368						
SR-480		29.95 %				
CD-540						
SR-399						
SR-239					2.0 %	2.08 %
SR-506						
CR-73				17.2 %	16.9 %	10.0 %
PRO-629						
Tinuvin 770			290 ppm			
UV Absorber			0.173 %			
Thermoplast Blue	0.534 ppm	0.374 ppm	0.6 ppm	0.5 ppm	4.5 ppm	4.58 ppm
Thermoplast	0.019 ppm	0.0133 ppm	0.015 ppm	0.012 ppm	0.58 ppm	0.58 ppm
Red						
Mineral Oil			136 ppm			65 ppm
Photochromic Dye Mixture					470 ppm	507 ppm

Table 2

Ingredient	Formula 7	Formula 8	Formula 9	Formula 10	Formula 11	Formula 12	
Irgacure 819	531.2 ppm	462 ppm	565.9 ppm	226 ppm	443 ppm	294 ppm	
Irgacure 184	18.7 ppm			144 ppm			
CN 384	0.77 %	0.887 %	0.78%	0.40%	0.61%		
CN386	0.77 %	0.887 %	0.78 %	0.53 %	0.61 %		
SR-348	72.4 %	70.36 %	58.20 %	41.5 %	88.70 %		
SR-368	24.1 %	23.87 %	21.4 %	7.0 %			
SR-480							
CD-540		<u> </u>	18.7 %	0.74 %		97.76 %	
SR-399				46.8 %			
SR-239	1.86 %	3.65 %	20.1 %			2.00 %	
SR-506					10.0 %		
CR-73			20.1 %	2.9 %			
PRO-629	0.05 %						
Tinuvin 770							
UV Absorber							
Thermoplast Blue	0.567 ppm	3.62 ppm	0.70 ppm	0.255 ppm	0.6 ppm	4.3 ppm	
Thermoplast Red	0.0147 ppm	0.576 ppm	0.014 ppm	0.006 ppm	0.028 ppm	0.24 ppm	
Photochromic Dye Mixture		450 ppm					

Table 3

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Ingredient	Formula 13	Formula 14	Formula 15	Formula 16	Formula 17	Formula 18
Irgacure 819	760 ppm	620 ppm	289 ppm		105 ppm	343 ppm
Irgacure 184						
CN 384	-	0.73 %	0.34 %			0.475 %
CN 386		0.73 %	0.34 %	1.00 %	0.70 %	0.475 %
2-ITX					188 ppm	141 ppm
SR-348				89.00%	92.00 %	98.90 %
SR-368						
SR-480						
CD-540	97.57 %	96.20 %	99.28 %		0.34 %	
SR-399						
SR-239	2.30 %	2.30 %	0.01 %			
SR-506						
SR-444						
SR-454				10.00 %	6.9 %	
CR-73						
PRO-629						
Tinuvin 770						
UV Absorber						785 ppm
Thermoplast Blue	4.9 ppm	5.1 ppm	0.508 ppm		0.35 ppm	0.69 ppm
Thermoplast Red	0.276 ppm	0.285 ppm	0.022 ppm		0.002 ppm	0.034 ppm
Dioctyl-						125 ppm
phthalate						
Butyl stearate						
Photochromic	499 ppm					
Dye Mixture						

Table 4

Ingredient	Formula 19	Formula 20	Formula 21	Formula 22	Formula 23	Formula 24
Irgacure 819	490 ppm	635 ppm	610 ppm	735 ppm	320 ppm	600 ppm
Irgacure 184						
CN 384	0.680 %	0.746 %	0.705 %	0.60%		
CN 386	0.680 %	0.746 %	0.705 %	0.60%		
2-ITX						
SR-348	69.30 %					68.60 %
	09.30 %				74.0 %	22.10 %
SR-368					74.0 %	22.10 %
SR-480						
CD-540		98.45 %	92.60 %	98.50 %	1.0 %	1.97 %
SR-399						
SR-239		0.01 %	3.86 %	0.16 %		
SR-506				0.10%		
SR-444	29.30 %					
SR-454					25.0 %	7.40 %
CR-73						
PRO-629		0.007 %	2.06 %			
Tinuvin 770						
UV Absorber						
Thermoplast Blue	0.37 ppm	0.507 ppm	3.07 ppm	4.3 ppm	0.15 ppm	0.29 ppm
Thermoplast Red	0.013 ppm	0.0126 ppm	0.336 ppm	0.41 ppm	0.006 ppm	0.012 ppm
Dioctyl- phthalate						
Butyl stearate						
Photochromic Dye Mixture			442 ppm	497 ppm		

Table 5

Ingredient	Formula 25	Formula 26	Formula 27	Formula 28	Formula 29	Formula 30	Formula 31
Irgacure 819	650 ppm	464 ppm	557 ppm	448 ppm	460 ppm		
Irgacure 184							300 ppm
CN 384	0.650 %	0.70 %					
CN 386	0.650 %	0.70 %					
2-ITX						600 ppm	120 ppm
SR-348		39.10 %					
SR-368		13.00 %		19.60 %	20.70 %		
SR-480					10.70 %		
CD-540	88.96 %	41.90 %	1.60 %	1.30 %		99.94 %	99.96%
SR-399							
SR-239				-			
SR-506			98.30 %	79.00 %	67.24 %		
SR-444	9.70 %	4.60 %					
SR-454							
CR-73							
PRO-629							
Tinuvin 770							
UV Absorber							
Thermoplast Blue	0.566 ppm	0.52 ppm	0.24 ppm	0.19 ppm	0.467 ppm		
Thermoplast	0.02 ppm	0.013 ppm	0.01 ppm	0.008 ppm	0.024 ppm		
Red							
Dioctyl-							
phthalate							
Butyl stearate	75 ppm	35 ppm					
Photochromic							
Dye Mixture							

Table 6

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In one embodiment, plastic lenses may be formed by disposing a mid-index lens forming composition into the mold cavity of a mold assembly and irradiating the mold assembly with activating light. Coating materials may be applied to the mold members prior to filling the mold cavity with the lens forming composition.

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After filing the mold cavity of the mold assembly the mold assembly is preferably placed in the lens curing unit and subjected to activating light. Preferably, actinic light is used to irradiate the mold assembly. A clear polycarbonate plate may be placed between the mold assembly and the activating light source. The polycarbonate plate preferably isolates the mold assembly from the lamp chamber, thus preventing airflow from the lamp cooling fans from interacting with the mold assemblies. The activating light source may be configured to deliver from about 0.1 to about 10 milliwatts/cm2 to at least one non-casting face, preferably both non-casting faces, of the mold assembly. Depending on the components of the lens forming composition used the intensity of activating light used may be <1 milliwatt/cm². The intensity of incident light at the plane of the lens curing unit drawer is measured using an International Light IL-1400 radiometer equipped with an XRL140A detector head. This particular radiometer preferably has a peak detection wavelength at about 400 nm, with a detection range from about 310 nm to about 495 nm. The International Light IL-1400 radiometer and the XRL140A detector head are both commercially available International Light, Incorporated of Newburyport, Massachusetts.

After the mold assembly is placed within the lens curing unit, the mold assemblies are preferably irradiated with activating light continuously for 30 seconds to thirty minutes, more preferably from one minute to five minutes. Preferably, the mold assemblies irradiated in the absence of a cooling air stream. After irradiation, the mold assemblies were removed from the lens curing unit and the formed lens demolded. The lenses may be subjected to a post-cure treatment in the post-cure unit.

In general, it was found that the use of a photoinitiator (e.g., IRG-819 and IRG-184) in the lens forming composition produces lenses with better characteristics than lens formed using a co-initiator only. For example, formula 15, described in the Table 4, includes a monomer composition (a mixture of SR-348 and SR-454) and a co-initiator (CN-386). When this lens forming composition was exposed to activating light for 15 min. there was no significant reaction or gel formation. It is believed that the co-initiator requires an initiating species in order to catalyze curing of the monomer composition. Typically this initiating species is produced from the reaction of the photoinitiator with activating light.

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A variety of photoinitiators and photoinitiators combined with co-initiators may be used to initiate polymerization of the monomer composition. One initiator system which may be used includes photoinitiators IRG-819 and 2-ITX and a co-initiator, see Formulas 17-18. Such a system is highly efficient at initiating polymerization reactions. The efficiency of a polymerization catalyst is a measurement of the amount of photoinitiator required to initiate a polymerization reaction. A relatively small amount of an efficient photoinitiator may be required to catalyze a polymerization reaction, whereas a greater amount of a less efficient photoinitiator may be required to catalyze the polymerization reaction. The IRG-819/2-ITX/co-initiator system may be used to cure lenses forming compositions which include a UV absorbing compound. This initiator system may also be used to form colored lenses.

An initiator system that is less efficient than the IRG-819/2-ITX/co-initiator system includes a mixture of the photoinitiators IRG-819 and 2-ITX, see Formula 31. This system is less efficient at initiating polymerization of lens forming compositions than the IRG-819/2-ITX/co-initiator system. The IRG-819/2-ITX system may be used to cure very reactive monomer compositions. An initiator system having a similar efficiency to the IRG-819/2-ITX system includes a mixture of IRG-819 and co-initiator, see Formulas 1-6, 8-9, 11, 14-15, 19-22, and 25-26. The IRG-819/co-initiator system

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may be used to cure clear lenses which do not include a UV blocking compound and photochromic lens forming compositions.

Another initiator system which may be used includes the photoinitiator 2-ITX and a co-initiator. This initiator system is much less efficient at initiating polymerization reactions than the IRG-819/co-initiator system. The 2-ITX/co-initiator system is preferably used for curing monomer compositions which include highly reactive monomers.

The use of the above described mid-index lens forming compositions may minimize or eliminate a number of problems associated with activating light curing of lenses. One problem typical of curing eyeglass lenses with activating light is pre-release. Pre-release may be caused by a number of factors. If the adhesion between the mold faces and the shrinking lens forming composition is not sufficient, pre-release may occur. The propensity of a lens forming composition to adhere to the mold face, in combination with its shrinkage, determine how the process variables are controlled to avoid prerelease. Adhesion is affected by such factors as geometry of the mold face (e.g., high-add flat-top bifocals tend to release because of the sharp change in cavity height at the segment line), the temperature of the mold assembly, and the characteristics of the inmold coating material. The process variables which are typically varied to control prerelease include the application of cooling fluid to remove exothermic heat, controlling the rate of heat generation by manipulating the intensities and timing of the activating radiation, providing differential light distribution across the thin or thick sections of the mold cavity manipulating the thickness of the molds, and providing in-mold coatings which enhance adhesion. An advantage of the above described mid-index lens forming compositions is that the composition appears to have enhanced adhesion characteristics. This may allow acceptable lenses to be produced over a greater variety of curing conditions. Another advantage is that higher diopter lenses may be produced at relatively low pre-release rates, broadening the achievable prescription range.

Another advantage of the above described mid-index lens forming compositions is that they tend to minimize problems associated with dripping during low intensity curing of lenses (e.g., in the 1 to 6 milliwatt range). Typically, during the irradiation of the lens forming composition with activating light, small amounts of monomer may be squeezed out of the cavity and run onto the non-casting faces of the molds. Alternatively, during filling of the mold assembly with the lens forming composition, a portion of the lens forming composition may drip onto the non-casting faces of the mold assembly. This "dripping" onto the non-casting faces of the mold assembly tends to cause the activating light to focus more strongly in the regions of the cavity located underneath the drippings. This focusing of the activating light may affect the rate of curing. If the rate of curing underneath the drippings varies significantly from the rate of curing throughout the rest of the lens forming composition, optical distortions may be created in the regions below the drippings.

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It is believed that differences in the rate of gelation between the center and the edge regions of the lens forming composition may cause dripping to occur. During the curing of a lens forming composition, the material within the mold cavity tends to swell slightly during the gel phase of the curing process. If there is enough residual monomer around the gasket lip, this liquid will tend to be forced out of the cavity and onto the non-casting faces of the mold. This problem tends to be minimized when the lens forming composition undergoes fast, uniform gelation. Typically, a fast uniform gelation of the lens forming composition may be achieved by manipulating the timing, intensities, and distribution of the activating radiation. The above described mid-index lens forming compositions, however, tend to gel quickly and uniformly under a variety of curing conditions, thus minimizing the problems caused by dripping.

Another advantage of the above described mid-index lens forming compositions is that the compositions tend to undergo uniform curing under a variety of curing

conditions. This uniform curing tends to minimize optical aberrations within the formed lens. This is especially evident during the formation of high plus power flattop lenses which tend to exhibit optical distortions after the lens forming composition is cured. It is believed that the activating radiation may be reflected off of the segment line and create local differences in the rate of gelation in the regions of the lens forming composition that the reflected light reaches. The above described mid-index lens forming compositions tend to show less optical distortions caused by variations of the intensity of activating radiation throughout the composition.

Other advantages include drier edges and increased rigidity of the formed lens.

An advantage of drier edges is that the contamination of the optical faces of the lens by uncured or partially cured lens forming composition is minimized.

METHODS OF FORMING PLASTIC LENSES

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Plastic lenses may be formed by disposing a lens forming composition into the mold cavity of a mold assembly and irradiating the mold assembly with activating light. Coating materials may be applied to the mold members prior to filling the mold cavity with the lens forming composition. The lens may be treated in a post-cure unit after the lens-curing process is completed.

The operation of the above described system to provide plastic lenses involves a number of operations. These operations are preferably coordinated by the controller 50, which has been described above. After powering the system, an operator is preferably signaled by the controller to enter the prescription of the lens, the type of lens, and the type of coating materials for the lens. Based on these inputted values the controller will preferably indicate to the operator which molds and gaskets will be required to form the particular lens.

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After obtaining the appropriate mold members the mold members are preferably cleaned prior to loading with a lens forming composition. The inner surface (i.e., casting surface) of the mold members may be cleaned on a spin coating unit 20 by spraying the mold members with a cleaning solution while spinning the mold members. Examples of cleaning solutions include methanol, ethanol, isopropyl alcohol, acetone, methyl ethyl ketone, or a water based detergent cleaner. Preferably, a cleaning solution which includes isopropyl alcohol is used to clean the mold members. As the mold member is contacted with the cleaning solution, dust and dirt may be removed and transferred into the underlying dish 115 of the curing unit. After a sufficient amount of cleaning solution has been applied the mold members may be dried by continued spinning without the application of cleaning solution.

In an embodiment, the inner surface, i.e., the casting face, of the front mold member may be coated with one or more hardcoat layers before the lens forming composition is placed within the mold cavity. Preferably, two hardcoat layers are used so that any imperfections, such as pin holes in the first hardcoat layer, are covered by the second hardcoat layer. The resulting double hardcoat layer is preferably scratch resistant and protects the subsequently formed eyeglass lens to which the double hardcoat layer adheres. The hardcoat layers are preferably applied using a spin coating unit 20. The mold member is preferably placed in the spin coating unit and the coating material applied to the mold while spinning at high speeds (e.g., between about 900 to 1000 RPM). After a sufficient amount of coating material has been applied, the coating material may be cured by the activating light source disposed in the cover. The cover is preferably closed and activating light is preferably applied to the mold member while the mold member is spinning at relatively low speeds (e.g., between about 150 to 250 RPM). Preferably control of the spinning and the application of activating light is performed by controller 50. Controller 50 is preferably configured to prompt the operator to place the mold members on the coating unit, apply the coating material to the mold member, and close the cover to initiate curing of the coating material.

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In an embodiment, the eyeglass lens that is formed may be coated with a hydrophobic layer, e.g. a hardcoat layer. The hydrophobic layer preferably extends the life of the photochromic pigments near the surfaces of the lens by preventing water and oxygen molecules from degrading the photochromic pigments.

In a preferred embodiment, both mold members may be coated with a cured adhesion-promoting composition prior to placing the lens forming composition into the mold cavity. Providing the mold members with such an adhesion-promoting composition is preferred to increase the adhesion between the casting surface of the mold and the lens forming composition. The adhesion-promoting composition thus reduces the possibility of premature release of the lens from the mold. Further, it is believed that such a coating also provides an oxygen and moisture barrier on the lens which serves to protect the photochromic pigments near the surface of the lens from oxygen and moisture degradation. Yet further, the coating provides abrasion resistance, chemical resistance, and improved cosmetics to the finished lens.

In an embodiment, the casting face of the back mold member may be coated with a material that is capable of being tinted with dye prior to filling the mold cavity with the lens forming composition. This tintable coat preferably adheres to the lens forming composition so that dyes may later be added to the resulting eyeglass lens for tinting the lens. The tintable coat may be applied using the spin coating unit as described above.

The controller may prompt the user to obtain the appropriate lens forming composition. In one embodiment, the controller will inform the user of which chemicals and the amounts of each chemical that is required to prepare the lens forming composition. Alternatively, the lens forming compositions may be preformed. In this case the controller may indicate to the operator which of the preformed lens forming compositions should be used.

In an embodiment, dyes may be added to the lens forming composition. It is believed that certain dyes may be used to attack and encapsulate ambient oxygen so that the oxygen may be inhibited from reacting with free radicals formed during the curing process. Also, dyes may be added to the composition to alter the color of an unactivated photochromic lens. For instance, a yellow color that sometimes results after a lens is formed may be "hidden" if a blue-red or blue-pink dye is present in the lens forming composition. The unactivated color of a photochromic lens may also be adjusted by the addition of non-photochromic pigments to the lens forming composition.

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In a preferred technique for filling the lens molding cavity 382 (see Fig. 11), the annular gasket 380 is placed on a concave or front mold member 392 and a convex or back mold member 390 is moved into place. The annular gasket 380 is preferably pulled away from the edge of the back mold member 390 at the uppermost point and a lens forming composition is preferably injected into the lens molding cavity 382 until a small amount of the lens forming composition is forced out around the edge. The excess is then removed, preferably, by vacuum. Excess liquid that is not removed could spill over the face of the back mold member 390 and cause optical distortion in the finished lens.

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The mold assembly, with a lens forming composition disposed within the mold cavity, is preferably placed within the lens curing unit. Curing of the lens forming composition is preferably initiated by the controller after the lens curing unit door is closed. The curing conditions are preferably set by the controller based on the prescription and type of lens being formed.

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After the curing cycle has been completed. The controller preferably prompts the user to remove the mold assembly from the lens curing unit. In an embodiment, the cured lens may be removed from the mold apparatus. The cured lens may be complete at this stage and ready for use.

In another embodiment, the cured lens may require a post cure treatment. After the lens is removed from the mold apparatus the edges of the lens may be dried and scraped to remove any uncured lens forming composition near the edges. The controller may prompt the user to place the partially cured lens into a post-cure unit. After the lens has been placed within the post-cure unit the controller may apply light and/or heat to the lens to complete the curing of the lens. In an embodiment, partially cured lenses may be heated to about 115 °C while being irradiated with activating light. This post-treatment may be applied for about 5 minutes.

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When casting a lens, particularly a positive lens that is thick in the center, cracking may be a problem. Addition polymerization reactions, including photochemical addition polymerization reactions, may be exothermic. During the process, a large temperature gradient may build up and the resulting stress may cause the lens to crack. Yellowing of the finished lens may also be a problem. Yellowing tends to be related to the monomer composition, the identity of the photoinitiator, and the concentration of the photoinitiator.

The formation of optical distortions usually occurs during the early stages of the polymerization reaction during the transformation of the lens forming composition from the liquid to the gel state. Once patterns leading to optical distortions form they may be difficult to eliminate. When gelation occurs there typically is a rapid temperature rise. The exothermic polymerization step causes a temperature increase, which in turn causes an increase in the rate of polymerization, which causes a further increase in temperature. If the heat exchange with the surroundings is not sufficient to cool the lens, there will be a runaway situation that leads to premature release, the appearance of thermally caused striations and even breakage.

Accordingly, when continuous activating light is applied, it is preferred that the

reaction process be smooth and not too fast but not too slow. Heat is preferably not generated by the process so fast that it may not be exchanged with the surroundings. The incident activating light intensity is preferably adjusted to allow the reaction to proceed at a desired rate. It is also preferred that the seal between the annular gasket 380 and the opposed mold members 378 be as complete as possible.

Factors that have been found to lead to the production of lenses that are free from optical distortions may be (1) achieving a good seal between the annular gasket 380 and the opposed mold members 378; (2) using mold members 378 having surfaces that are free from defects; (3) using a formulation having an appropriate type and concentration of photoinitiator that will produce a reasonable rate of temperature rise; and (4) using a homogeneous formulation. Preferably, these conditions are optimized.

Premature release of the lens from the mold will result in an incompletely cured lens and the production of lens defects. Factors that contribute to premature release may be (1) a poorly assembled mold assembly 352; (2) the presence of air bubbles around the sample edges; (3) imperfection in gasket lip or mold edge; (4) inappropriate formulation; (5) uncontrolled temperature rise; and (6) high or non-uniform shrinkage. Preferably, these conditions are minimized.

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Premature release may also occur when the opposed mold members 378 are held too rigidly by the annular gasket 380. Preferably, there is sufficient flexibility in the annular gasket 380 to permit the opposed mold members 378 to follow the lens as it shrinks. Indeed, the lens must be allowed to shrink in diameter slightly as well as in thickness. The use of an annular gasket 380 that has a reduced degree of stickiness with the lens during and after curing is therefore desirable.

Despite the above problems, the advantages offered by the radiation cured lens molding system clearly outweigh the disadvantages. The advantages of a radiation cured

system include a significant reduction in energy requirements, curing time and other problems normally associated with conventional thermal systems.

1. Method of Forming a Plastic Lens by Curing with Activating Light.

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In one embodiment, plastic lenses may be formed by disposing a lens forming composition into the mold cavity of a mold assembly and irradiating the mold assembly with activating light. Coating materials may be applied to the mold members prior to filling the mold cavity with the lens forming composition. The lens may be treated in a post-cure unit after the lens-curing process is completed.

The lens forming composition is preferably prepared according to the following protocol. Appropriate amounts of HDDMA, TTEGDA, TMPTA and TRPGDA are mixed and stirred thoroughly, preferably with a glass rod. The acrylate/methacrylate mixture may then be passed through a purification column.

A suitable purification column may be disposed within a glass column having a fitted glass disk above a Teflon stopcock and having a top reservoir with a capacity of approximately 500 ml and a body with a diameter of 22 mm and a length of about 47 cm. The column may be prepared by placing on the fitted glass disk approximately 35 g. of activated alumina (basic), available from ALFA Products, Johnson Matthey, Danvers, MA in a 60 mesh form or from Aldrich in a 150 mesh form. Approximately 10 g. of an inhibitor remover (hydroquinone/methylester remover) available as HR-4 from Scientific Polymer Products, Inc., Ontario, NY then may be placed on top of the alumina and, finally, approximately 35 g. of activated alumina (basic) may be placed on top of the inhibitor remover.

Approximately 600 g. of the acrylate/methacrylate mixture may then be added above the column packing. An overpressure of 2-3 psi may then be applied to the top of

the column resulting in a flow rate of approximately 30 to 38 grams per hour. Parafilm may be used to cover the junction of the column tip and the receiving bottle to prevent the infiltration of dust and water vapor. The acrylate/methacrylate mixture, preferably, may be received in a container that is opaque to activating light.

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An appropriate amount of bisphenol A bis(allyl carbonate) may then be added to the acrylate/methacrylate mixture to prepare the final monomer mixture.

An appropriate amount of a photoinitiator may then be added to the final monomer mixture. The final monomer mixture, with or without photoinitiator, may then be stored in a container that is opaque to activating light.

An appropriate amount of a dye may also be added to the final monomer mixture, with or without photoinitiator.

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After filling the mold cavity with the lens forming composition, the mold assembly is preferably irradiated with activating light. In one embodiment, the lamps generate an intensity at the lamp surface of approximately 4.0 to 7.0 mW/cm² of ultraviolet light having wavelengths between 300 and 400 nm, which light is very uniformly distributed without any sharp discontinuities throughout the reaction process. Such bulbs are commercially available from Sylvania under the trade designation Sylvania Fluorescent (F15T8/2052) or Sylvania Fluorescent (F15T8/350BL/18") GTE. Activating light having wavelengths between 300 and 400 nm is preferred because the photoinitiators preferably absorb most efficiently at this wavelength and the mold members 378, preferably, allow maximum transmission at this wavelength. It is preferred that there be no sharp intensity gradients of activating light either horizontally or vertically through the lens composition during the curing process. Sharp intensity gradients through the lens may lead to defects in the finished lens.

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If lenses are produced with continuous activating light without any mold cooling, the temperature of the mold-lens assembly may rise to above 50°C. Low diopter lenses may be prepared in this fashion, but higher plus or minus diopter lenses may fail. Certain lenses may be made by controlling (e.g., cooling) the temperature of the lens material during cure with circulating uncooled fluid (i.e., fluid at ambient temperatures). The ambient fluid in these systems is preferably directed towards the mold members in the same manner as described above. Circulating ambient temperature fluid permits manufacture of a wider range of prescriptions than manufacture of the lenses without any mold cooling at all.

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Many polymerization factors may be interrelated. The ideal temperature of polymerization is typically related to the diopter and thickness of the lens being cast. Lower temperatures (below about 10°C) are preferred to cast higher + or - diopter lenses when using continuous activating light. These lower temperatures tend to permit an increase in photoinitiator concentration, which in turn may speed up the reaction and lower curing time.

Preventing premature release when using continuous activating light may also be somewhat dependent upon the flow rates of cooling fluid, as well as its temperature. For instance, if the temperature of the cooling fluid is decreased it may also be possible to decrease the flowrate of cooling fluid. Similarly, the disadvantages of a higher temperature cooling fluid may be somewhat offset by higher flow rates of cooling fluid.

In one embodiment the air flow rates for a dual distributor system (i.e., an air distributor above and below the lens composition) are about 1-30 standard cubic feet ("scf") (about 0.028 - 0.850 standard cubic meters, "scm") per minute per distributor, more preferably about 4-20 scf (about 0.113-0.566 scm) per minute per distributor, and more preferably still about 9-15 scf (about 0.255-0.423 scm) per minute per distributor. "Standard conditions," as used herein, means 60 °F (about 15.5 °C) and one atmosphere

pressure (about 101 kilopascals).

The thickness of the glass molds used to cast polymerized lenses may affect the lenses produced. A thinner mold tends to allow more efficient heat transfer between the polymerizing material and the cooling air, thus reducing the rate of premature release. In addition, a thinner mold tends to exhibit a greater propensity to flex. A thinner mold tends to flex during the relatively rapid differential shrinkage between the thick and thin portions of a polymerized lens, again reducing the incidence of premature release. In one embodiment the first or second mold members have a thickness less than about 5.0 mm, preferably about 1.0-5.0 mm, more preferably about 2.0-4.0 mm, and more still about 2.5-3.5 mm.

"Front" mold or face means the mold or face whose surface ultimately forms the surface of an eyeglass lens that is furthest from the eye of an eyeglass lens wearer.

"Back" mold or face means the mold or face whose surface ultimately forms the surface of an eyeglass lens that is closest to the eye of an eyeglass lens wearer.

In one embodiment, the lens forming material is preferably cured to form a solid lens at relatively low temperatures, relatively low continuous activating light intensity, and relatively low photoinitiator concentrations. Lenses produced as such generally have a Shore D hardness of about 60-78 (for preferred compositions) when cured for about 15 minutes as described above. The hardness may be improved to about 80-81 Shore D by postcure heating the lens in a conventional oven for about 10 minutes, as described above.

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The activating light cured lenses may demonstrate excellent organic solvent resistance to acetone, methyl ethyl ketone, and alcohols.

2. Preparing Lenses of Various Powers By Altering the Lens Forming Conditons.

It has been determined that in some embodiments the finished power of an activating light polymerized lens may be controlled by manipulating the curing temperature of the lens forming composition. For instance, for an identical combination of mold members and gasket, the focusing power of the produced lens may be increased or decreased by changing the intensity of activating light across the lens mold cavity or the faces of the opposed mold members.

As the lens forming material begins to cure, it passes through a gel state, the pattern of which, within the mold assembly, leads to the proper distribution of internal stresses generated later in the cure when the lens forming material begins to shrink. As the lens forming material shrinks during the cure, the opposed mold members will preferably flex as a result of the different amounts of shrinkage between the relatively thick and the relatively thin portions of the lens. When a negative lens, for example, is cured, the upper or back mold member will preferably flatten and the lower or front mold member will preferably steepen with most of the flexing occurring in the lower or front mold member. Conversely, with a positive lens, the upper or back mold member will preferably flatten with most of the flexing occurring in the lower or front mold member will preferably flatten with most of the flexing occurring in the upper or back mold member.

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By varying the intensity of the activating light between the relatively thin and the relatively thick portions of the lens in the lens forming cavity, it is possible to create more or less total flexing. Those light conditions which result in less flexing will tend to minimize the possibility of premature release.

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The initial curvature of the opposed mold members and the center thickness of the lens produced may be used to compute the targeted power of the lens. Herein, the "targeted power" of a lens is the power a lens may have if the lens were to have a curvature and thickness substantially identical to the mold cavity formed by the opposed

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mold members. The activating light conditions may be manipulated to alter the power of the lens to be more or less than the targeted power.

By varying the amount of activating light reaching the lens mold the polymerization rate, and therefore the temperature of the lens forming composition may be controlled. It has been determined that the maximum temperature reached by the lens forming composition during and/or after activation by light may effect the final power of the lens. By allowing the lens forming composition to reach a temperature higher than the typical temperatures described in previous embodiments, but less than the temperature at which the formed lens will crack, the power of the lens may be decreased. Similarly, controlling the polymerization such that the temperature of the lens forming composition remains substantially below the typical temperatures described in previous embodiments, but at a sufficient temperature such that a properly cured lens is formed, the power of the lens may be increased. Similarly, increasing the temperature of the lens forming composition during curing may decrease the power of the resulting lens.

In an embodiment, an ophthalmic eyeglass lens may be made from a lens forming composition comprising a monomer and a photoinitiator, by irradiation of the lens forming composition with activating light. The composition may optionally include one or more of: an ultraviolet/visible light absorbing compound, a polymerization inhibitor, a co-initiator, a hindered amine light stabilizer, and a dye. The activating light may include ultraviolet, actinic, visible or infrared light. The lens forming composition may be treated with activating light such that an eyeglass is formed that has a power substantially equal to the targeted power for a given mold cavity. The peak temperature of the lens forming process may be the maximum temperature attained after the application of each pulse of activating light. As depicted in Fig. 40, each pulse of activating light may cause the lens forming composition to rise to a peak temperature.

After reaching this peak temperature the lens forming composition may begin to

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cool until the next application of activating light. If the peak temperature of the lens forming composition is controlled such that the formed lens has a power substantially equal to the targeted power, the peak temperature is referred to as the "matching temperature". The matching temperature may be determined by performing a series of experiments using the same mold cavity. In these experiments the peak temperature attained during the process is preferably varied. By measuring the power of the lenses obtained through this experiment the matching temperature range may be determined.

When the temperature of the lens forming composition is allowed to rise above the matching temperature during treatment with activating light, the power of the lens may be substantially less than the targeted power of the lens. Alternatively, when the temperature of the lens forming composition is allowed to remain below the matching temperature, the power of the lens may be substantially greater than the targeted power of the lens. In this manner, a variety of lenses having substantially different lens powers from the targeted power may be produced from the same mold cavity.

When the lenses cured by the activating light are removed from the opposed mold members, they are typically under a stressed condition. It has been determined that the power of the lens may be brought to a final resting power, by subjecting the lenses to a post-curing heat treatment to relieve the internal stresses developed during the cure and cause the curvature of the front and the back of the lens to shift. Typically, the lenses may be cured by the activating light in about 10-30 minutes (preferably about 15 minutes). The post-curing heat treatment is preferably conducted at approximately 85-120 °C for approximately 5-15 minutes. Preferably, the post-curing heat treatment is conducted at 100-110 °C for approximately 10 minutes. Prior to the post-cure, the lenses generally have a lower power than the final resting power. The post-curing heat treatment reduces yellowing of the lens and reduces stress in the lens to alter the power thereof to a final resting power.

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In an embodiment, an ophthalmic eyeglass lens may be made from a lens forming composition comprising a monomer and a photoinitiator, by irradiation of the lens forming composition with activating light. The composition may optionally include one or more of: an ultraviolet/visible light absorbing compound, a polymerization inhibitor, a co-initiator, a hindered amine light stabilizer, and a dye. The activating light may include ultraviolet, actinic, visible or infrared light. The lens forming composition may be treated with activating light such that an eyeglass is formed. The lens may be kept within the mold cavity formed by the mold members until the light has completely cured the lens forming composition. The minimum time which a lens must remain in the mold cavity to produce a lens with the targeted power, with respect to the mold cavity, is herein referred to as the "demolding time". The demolding time may be determined by performing a series of experiments using the same mold cavity. In these experiments the time that the lens is released from the mold cavity during the process is preferably varied. By measuring the power of the lenses obtained through these experiments the demolding time range may be determined.

When a formed lens is removed prior to the demolding time, the power of the lens may be substantially greater than the targeted power of the lens. By varying the demolding time a variety of lenses having substantially greater lens powers from the targeted power may be produced from the same mold cavity.

3. Postcure With An Oxygen Barrier Enriched With Photoinitiator

In certain applications, all of the lens forming composition may fail to completely cure by exposure to activating light when forming the lens. In particular, a portion of the lens forming composition proximate the gasket often remains in a liquid state following formation of the lens. It is believed that the gaskets may be often somewhat permeable to air, and, as a result, oxygen permeates them and contacts the portions of the lens forming material that are proximate the gasket. Since oxygen tends to inhibit the polymerization

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process, portions of the lens forming composition proximate the gasket tend to remain uncured as the lens is formed.

Uncured lens forming composition proximate the gasket may be a problem for several reasons. First, the liquid lens forming composition leaves the edges of the cured lens in a somewhat sticky state, which makes the lenses more difficult to handle. Second, the liquid lens forming composition may be somewhat difficult to completely remove from the surface of the lens. Third, liquid lens forming composition may flow and at least partially coat the surface of lenses when such lenses are removed from the molds. This coating may be difficult to remove and makes application of scratch resistant coatings or tinting dyes more difficult. This coating tends to interfere with the interaction of scratch resistant coatings and tinting dyes with the cured lens surface. Fourth, if droplets of liquid lens forming material form, these droplets may later cure and form a ridge or bump on the surface of the lens, especially if the lens undergoes later postcure or scratch resistant coating processes. As a result of the above problems, often lenses must be tediously cleaned or recast when liquid lens forming composition remains after the lens is formed in an initial cure process.

The problems outlined above may be mitigated if less liquid lens forming composition remains proximate the gasket after the lens is formed. One method of lessening this "wet edge" problem relates to increasing the amount of photoinitiator present in the lens forming composition (i.e., increasing the amount of photoinitiator in the lens forming composition above about 0.15 percent). Doing so, however, tends to create other problems. Specifically, increased photoinitiator levels tend to cause exothermic heat to be released at a relatively high rate during the reaction of the composition. Premature release and/or lens cracking tends to result. Thus it is believed that lower amounts of photoinitiator are preferred.

The wet edge problem has been addressed by a variety of methods described in

U.S. Patent No. 5,529,728 to Buazza et. al. Such methods relate to removing the gasket and applying either an oxygen barrier or a photoinitiator enriched liquid to the exposed edge of the lens. The lens is preferably re-irradiated with sufficient activating light to completely dry the edge of the lens prior to demolding.

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An embodiment relates to improving the methods described in U.S. Patent No. 5,529,728 to Buazza et. al. This embodiment relates to combining an oxygen barrier with a photoinitiator. Specifically, in one embodiment an oxygen barrier 970 (e.g., a thin strip of polyethylene film or the like as shown in Fig. 12) is preferably embedded or impregnated with a photoinitiator 972. The oxygen barrier is preferably wrapped around the edge of a cured lens which is still encased between two molds (but with the gasket removed). While still "in the mold," the lens is preferably exposed to activating light, thereby drying its edge. An improvement of this method over those previously disclosed is that there may be a significant reduction in the dosage of activating light necessary to bring the lens edge to dryness.

A plastic oxygen barrier film which includes a photoinitiator may be made by: (a) immersing a plastic film in a solution comprising a photoinitiator, (b) removing the plastic film from the solution, and (c) drying the plastic film. The solution may include an etching agent. Preferably a surface of the plastic film is etched prior to or while immersing the plastic film in the solution.

In one example, thin strips (e.g., about 10 mm wide) of high density polyethylene film (approximately 0.013 mm thick) may be soaked in a solution of 97% acetone and 3% Irgacure 184 (a photoinitiator commercially available from Ciba Geigy located in Farmingdale, New Jersey) for about five minutes. The polyethylene film may be obtained from Tape Solutions, Inc. (Nashville, Tennessee). In a more preferred embodiment, 0.5% BYK-300 (a flow agent commercially available from BYK Chemie located in Wallingford, Connecticut) may be included in the soaking solution. It is believed that xylene in the BYK-300 tends to etch the surface of the film and make the Atty. Dkt. No.: 5040-04200 128 Conley, Rose & Tayon, P.C.

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film more receptive to absorption of the Irgacure 184. In a still more preferred embodiment, the treated polyethylene strips may be dipped in acetone for about ten seconds to remove excess Irgacure 184. Excess photoinitiator may be seen as a white powder which coats the strips after drying. In either case, the strips are preferably allowed to air dry before applying them to the edge of the lens as described above.

In one alternate embodiment, a plastic eyeglass lens may be made by the following steps: (1) placing a liquid polymerizable lens forming composition in a mold cavity defined by a gasket, a first mold member, and a second mold member; (2) directing first activating light rays toward at least one of the mold members to cure the lens forming composition so that it forms a lens with a back face, edges, and a front face, and wherein a portion of the lens forming composition proximate the edges of the lens is not fully cured; (3) removing the gasket to expose the edges of the lens; (4) applying an oxygen barrier which includes a photoinitiator around the exposed edges of the lens such that at least a portion of the oxygen barrier photoinitiator is proximate lens forming composition that is not fully cured; and (5) directing second activating light rays towards the lens such that at least a portion of the oxygen barrier photoinitiator initiates reaction of lens forming composition while the oxygen barrier substantially prevents oxygen from outside the oxygen barrier from contacting at least a portion of the lens forming composition. The first and second activating light rays may (a) be at the same or different wavelengths and/or intensities, (b) be continuous or pulsed, and (c) be from the same or different light source.

A purpose of the steps 4-5 is to reduce the amount of uncured liquid lens forming composition that is present when the lens is separated from the molds and/or gasket. It has been found that reducing the amount of liquid lens forming composition may be especially advantageous if such reduction occurs before the molds are separated from the cured lens. Separating the molds from the cured lens may cause uncured liquids to at least partially coat the lens faces. This coating may occur when uncured liquid lens

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forming composition gets swept over the faces when the molds are separated from the lens. It is believed that curing of the lens tends to create a vacuum between the lens and the mold. Air may sweep over the mold faces to fill this vacuum when the molds are separated from the lens. This air tends to take liquid lens forming composition into the vacuum with it.

In step 4 above, an oxygen barrier which includes a photoinitiator is preferably applied to the edges or sides of the lens after the gasket is removed. Preferably, this oxygen barrier is applied while the lens is still attached to the molds. In an alternate embodiment, this oxygen barrier is preferably applied to the edges or sides of the molds at the same time it is applied to the sides of the lens. In a preferred embodiment, the sides of the lenses are first cleaned or wiped to remove at least a portion of the uncured liquid lens forming composition before the oxygen barrier is applied.

After the oxygen barrier is applied, second activating light rays may be directed towards the lens. After the second activating light rays are directed toward the lens, at least a portion of the liquid lens forming composition that was not cured in the initial cure steps may be cured. It is believed that the photoinitiator embedded in the oxygen barrier facilitates faster and more complete curing of the uncured lens forming composition. As such, less second activating light rays may be employed, thereby lessening the time and energy required in this step. Furthermore, lens quality tends to be enhanced since a lower application of the second activating light rays tends to reduce the potential for lens yellowing.

In a preferred embodiment, substantially all of the remaining liquid lens forming composition is cured after the second activating light rays are directed toward the lens. More preferably, the lens is substantially dry after the second activating light is directed towards the lens.

After the second activating light is directed toward the lens, the lens may then be
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demolded. The lens may then be tinted. After the lens is demolded, a scratch resistant coating may be applied to the lens. In one embodiment, a scratch resistant coating is preferably applied to the demolded lens by applying a liquid scratch resistant coating composition to a face of the lens and then applying activating light rays to this face to cure the liquid scratch resistant coating to a solid.

In an embodiment, the activating light for curing the scratch resistant coating is ultraviolet light. The intensity of the activating light applied to the face of the lens to cure the liquid scratch resistant coating composition to a solid is preferably about 150-300 mW/cm² at a wavelength range of about 360-370 nm, and about 50-150 mW/cm² at a wavelength range of about 250-260 nm. The lens may be heated after removal from the molds, or after application of a scratch resistant coating to the lens.

In a preferred embodiment, the above method may further include the additional step of directing third activating light rays towards the lens before the oxygen barrier is applied. These third activating light rays are preferably applied before the gasket is removed. Preferably, the second and third activating light rays are directed toward the back face of the lens (as stated above, the second and third activating light rays are preferably applied while this lens is in the mold cavity). The third activating light rays are preferably about the same range of intensity as the second activating light rays. The same apparatus may be used for both the second and third activating light rays.

In a preferred embodiment, the method described above also includes the step of removing the oxygen barrier from the edges of the lens.

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The second and third activating light rays may be repeatedly directed towards the lens. For instance, these activating light rays may be applied via a light assembly whereby the lens passes under a light source on a movable stand. The lens may be repeatedly passed under the lights. Repeated exposure of the lens to the activating light

rays may be more beneficial than one prolonged exposure.

Preferably the oxygen barrier includes a film, and more preferably a plastic, flexible, and/or elastic film. In addition, the oxygen barrier is preferably at least partially transparent to activating light so that activating light may penetrate the oxygen barrier to cure any remaining liquid lens forming composition. Preferably, the oxygen barrier is stretchable and self-sealing. These features make the film easier to apply. Preferably, the oxygen barrier is resistant to penetration by liquids, thus keeping any liquid lens forming composition in the mold assembly. Preferably, the oxygen barrier includes a thermoplastic composition. It is anticipated that many different oxygen barriers may be used (e.g., saran wrap, polyethylene, etc.). In one preferred embodiment, the film is "Parafilm M Laboratory Film" which is available from American National Can (Greenwich, CT, U.S.A.). The oxygen barrier may also include aluminum foil.

Preferably, the oxygen barrier is less than about 1.0 mm thick. More preferably, the oxygen barrier is 0.01 to 0.10 mm thick, and more preferably still, the oxygen barrier is less than 0.025 mm thick. If the oxygen barrier is too thick, then it may not be readily stretchable and/or conformable, and it may not allow a sufficient amount of light to pass through it. If the oxygen barrier is too thin, then it may tend to tear.

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In an alternate method, a lens may be cured between two mold members. The gasket may be removed and any remaining liquid lens composition may be removed. At this point a mold member may be applied to a substantially solid conductive heat source. Heat may then be conductively applied to a face of the lens by (a) conductively transferring heat to a face of a mold member from the conductive heat source, and (b) conductively transferring heat through such mold member to the face of the lens. The oxygen barrier enriched with photoinitiator may then be applied, and second activating light rays may be directed towards the lens to cure the remaining lens forming composition.

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4. Applying Coating Materials to Lenses

In an embodiment, coating apparatus 20 may be used to apply a pre-coat to a lens before the hardcoat is applied. The pre-coat may serve to increase the "wettability" of the surface to which the hardcoat is to be applied. A surfactant has been conventionally employed for this purpose, however surfactants tend to affect the volatility and flow characteristics of lens coatings in an unfavorable manner. The pre-coat may include acetone and/or BYK-300. Upon even distribution of the hardcoat onto a lens, the coating may be wiped near the edges of the lens to prevent the formation of excessive flakes during curing.

5. Curing by the Application of Pulsed Activating Light

A polymerizable lens forming composition may be placed in a mold/gasket assembly and continuously exposed to appropriate levels of activating light to cure the composition to an optical lens. The progress of the curing reaction may be determined by monitoring the internal temperature of the composition. The lens forming composition may be considered to pass through three stages as it is cured: (1) induction, (2) gel formation & exotherm, and (3) extinction. These stages are illustrated in Fig. 22 for a - .75 -1.00 power lens cured by continuous application of activating light. Fig. 22 shows temperature within the mold cavity as a function of time throughout a continuous radiation curing cycle.

The induction stage occurs at the beginning of the curing cycle and is typically characterized by a substantially steady temperature of the lens forming composition as it is irradiated with activating light (or falling temperature when the curing chamber temperature is below that of the composition). During the induction period, the lens forming composition remains in a liquid state as the photoinitiator breaks down and

consumes inhibitor and dissolved oxygen present in the composition. As the inhibitor content and oxygen content of the composition fall, decomposing photoinitiator and the composition begin to form chains to produce a pourable, "syrup-like" material.

As irradiation continues, the "syrup" proceeds to develop into a soft, non-pourable, viscous, gel. A noticeable quantity of heat will begin to be generated during this soft gel stage. The optical quality of the lens may be affected at this point. Should there be any sharp discontinuities in the intensity of the activating light (for example, a drop of composition on the exterior of a mold which focuses light into a portion of the lens forming composition proximate the drop), a local distortion will tend to be created in the gel structure, likely causing an aberration in the final product. The lens forming composition will pass through this very soft gel state and through a firm gel state to become a crystalline structure. When using OMB-91 lens forming composition, a haze tends to form momentarily during the transition between the gel and crystalline stages. As the reaction continues and more double bonds are consumed, the rate of reaction and the rate of heat generated by the reaction will slow, which may cause the internal temperature of the lens forming composition to pass through a maximum at the point where the rate of heat generation exactly matches the heat removal capacity of the system.

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By the time the maximum temperature has been reached and the lens forming composition begins to cool, the lens will typically have achieved a crystalline form and will tend to crack rather than crumble if it is broken. The rate of conversion will slow dramatically and the lens may begin to cool even though some reaction still may be occurring. Irradiation may still be applied through this extinction phase. Generally, the curing cycle is assumed to be complete when the temperature of the lens forming composition falls to a temperature near its temperature at the beginning of exotherm (i.e., the point where the temperature of the composition increased due to the heat released by the reaction).

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The continuous irradiation method tends to work well for relatively low mass lenses (up to about 20-25 grams, see, e.g., U.S. Patents 5,364,256 and 5,415,816). As the amount of material being cured increases, problems may be encountered. The total amount of heat generated during the exothermic phase is substantially proportional to the mass of the lens forming material. During curing of relatively high mass lenses, a greater amount of heat is generated per a given time than during curing of lower mass lenses. The total mold/gasket surface area available for heat transfer (e.g., heat removal from the lens forming composition), however, remains substantially constant. Thus, the internal temperature of a relatively high mass of lens forming material may rise to a higher temperature more rapidly than typically occurs with a lower mass of lens forming material. For example, the internal temperature of a low minus cast-to-finish lens typically will not exceed about 100 °F, whereas certain thicker semi-finished lens "blanks" may attain temperatures greater than about 350 °F when continually exposed to radiation. The lens forming material tends to shrink as curing proceeds and the release of excessive heat during curing tends to reduce the adhesion between the mold and the lens forming material. These factors may lead to persistent problems of premature release and/or cracking during the curing of lens forming material having a relatively high mass.

An advantage of the present method is the production of relatively high-mass, semi-finished lens blanks and high power cast-to-finish lenses without the above-mentioned problems of premature release and cracking. The methods described below allow even more control over the process of curing ophthalmic lenses with activating light-initiated polymerization than previous methods. By interrupting or decreasing the activating light at the proper time during the cycle, the rate of heat generation and release may be controlled and the incidence of premature release may be reduced. An embodiment relates to a method of controlling the rate of reaction (and therefore the rate of heat generation) of an activating light-curable, lens forming material by applying selected intermittent doses (e.g., pulses) of radiation followed by selected periods of

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decreased activating light or "darkness". It is to be understood that in the description that follows, "darkness" refers to the absence of activating radiation, and not necessarily the absence of visible light.

More particularly, an embodiment relates to: (a) an initial exposure period of the lens forming material to radiation (e.g., continuous or pulsed radiation) extending through the induction period, (b) interrupting or decreasing the irradiation before the material reaches a first temperature (e.g., the maximum temperature the composition could reach if irradiation were continued) and allowing the reaction to proceed to a second temperature lower than the first temperature, and (c) applying a sufficient number of alternating periods of exposure and decreased activating light or darkness to the lens forming material to complete the cure while controlling the rate of heat generation and/or dissipation via manipulation of the timing and duration of the radiation, or the cooling in the curing chamber. Fig. 23 shows the temperature within the mold cavity as a function of time for both (a) continuous activating light exposure and (b) pulsed activating light exposure.

In the context of this application, a "gel" occurs when the liquid lens forming composition is cured to the extent that it becomes substantially non-pourable, yet is still substantially deformable and substantially not crystallized.

In the following description, it is to be understood that the term "first period" refers to the length of time of the initial exposure period where radiation (e.g., in pulses) is applied to the lens forming composition, preferably to form at least a portion of the composition into a gel. "First activating" rays or light refers to the radiation applied to the lens forming composition during the initial exposure period. "Second activating" rays or light refers to the radiation that is applied to the lens forming composition (e.g., in pulses) after the composition has been allowed to cool to the "third temperature" mentioned above. "Second period" refers to the duration of time that second activating

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rays are directed to the lens forming composition. "Third period" refers to the duration of decreased activating light or darkness that ensues after activating light has been delivered in the second period.

In an embodiment, the lens forming material is preferably placed in a mold cavity defined in part between a first mold member and a second mold member. The first mold member and/or second mold member may or may not be continuously cooled as the formation of the lens is completed during the second period and/or third period. One method of removing heat from the lens forming material is to continuously direct air at a non-casting face of at least one of the mold members. It is preferred that air be directed at both the first and second mold members. A cooler may be used to cool the temperature of the air to a temperature below ambient temperature, more preferably between about 0 °C and about 20 °C, and more preferably still between about 3 °C and about 15 °C. Air may also be used to cool at least one of the mold members (in any of the manners described previously) during the first period.

In an embodiment, the first period ends when at least a portion of the lens forming composition begins to increase in temperature or form a gel, and the first activating rays are decreased or removed (e.g., blocked) such that they cease to contact the first or second mold members. It is preferred that the first period be sufficient to allow the lens forming material to gel in the mold cavity such that there is substantially no liquid present (except small amounts proximate the edge of the material). The interruption of irradiation prior to complete gellation may in some circumstances produce optical distortions. It is preferred that the length of the first period be selected to inhibit the lens forming composition from reaching a first temperature. The first temperature is preferably the maximum temperature that the lens forming composition could reach if it was irradiated under the system conditions (e.g., flow rate and temperature of any cooling air, wavelength and intensity of radiation) until the "exothermic potential" (i.e., ability to evolve heat through reaction) of the composition was exhausted.

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According to an embodiment, the reactions within the composition are preferably allowed to proceed after the first activating rays are removed until the composition reaches a second temperature. The second temperature is preferably less than the first temperature. The first temperature is preferably never reached by the composition. Thus, the composition is preferably prevented from achieving the first temperature and then cooling to the second temperature. The composition is preferably allowed to cool from the second temperature to the third temperature. This cooling may occur "inactively" by allowing heat to transfer to the ambient surroundings, or at least one of the mold members may be cooled by any of the methods described above.

In an embodiment, the curing of the lens forming material may be completed by directing second activating rays (e.g., in pulses) toward at least one of the mold members. The second activating rays may be directed toward the mold member(s) for a second period that may be determined according to the rate of reaction of the lens forming composition. The change in temperature of the composition or a portion of the mold cavity, or the air in or exiting the chamber may be an indicator of the rate of reaction, and the second period may be determined accordingly. The second period may be varied such that subsequent pulses have a longer or shorter duration than previous pulses. The time between pulses (i.e., the third period) may also be varied as a function of the temperature and/or reaction rate of the composition. To achieve a light pulse, (a) the power to a light source may be turned on and then off, (b) a device may be used to alternately transmit and then block the passage of light to the lens forming composition, or (c) the light source and/or mold assembly may be moved to inhibit activating light from contacting the lens forming material. The second and/or third periods are preferably controlled to allow rapid formation of a lens while reducing the incidence of (a) premature release of the lens from the first and/or second mold member and/or (b) cracking of the lens.

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In an embodiment, the second period is preferably controlled to inhibit the temperature of the composition from exceeding the second temperature. The temperature of the lens forming composition may continue to increase after radiation is removed from the first and/or second mold members due to the exothermic nature of reactions occurring within the composition. The second period may be sufficiently brief such that the pulse of second activating rays is removed while the temperature of the composition is below the second temperature, and the temperature of the composition increases during the third period to become substantially equal to the second temperature at the point that the temperature of the composition begins to decrease.

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In an embodiment, the third period extends until the temperature of the composition becomes substantially equal to the third temperature. Once the temperature of the composition decreases to the third temperature, a pulse of second activating rays may be delivered to the composition. In an embodiment, the second period remains constant, and the third period is preferably controlled to maintain the temperature of the composition below the second temperature. The third period may be used to lower the temperature of the composition to a temperature that is expected to cause the composition to reach but not exceed the second temperature after a pulse is delivered to the composition.

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In an embodiment, a shutter system may be used to control the application of first and/or second activating rays to the lens forming material. The shutter system preferably includes air-actuated shutter plates that may be inserted into the curing chamber to prevent activating light from reaching the lens forming material.

Alternatively, the shutter system may include an LCD panel. Controller 50 may receive signals from thermocouple(s) located inside the lens-curing chamber, proximate at least a portion the mold cavity, or located to sense the temperature of air in or exiting the chamber, allowing the time intervals in which the shutters are inserted and/or extracted to

be adjusted as a function of a temperature within the curing chamber. The thermocouple may be located at numerous positions proximate the mold cavity and/or casting chamber.

The wavelength and intensity of the second activating rays are preferably substantially equal to those of the first activating rays. It may be desirable to vary the intensity and/or wavelength of the radiation (e.g., first or second activating rays). The particular wavelength and intensity of the radiation employed may vary among embodiments according to such factors as the identity of the composition and curing cycle variables.

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Numerous curing cycles may be designed and employed. The design of an optimal cycle should include consideration of a number of interacting variables. Significant independent variables include: 1) the mass of the sample of lens forming material, 2) the intensity of the light applied to the material, 3) the physical characteristics of the lens forming material, and 4) the cooling efficiency of the system. Significant curing cycle (dependent) variables include: 1) the optimum initial exposure time for induction and gelling, 2) the total cycle time, 3) the time period between pulses, 4) the duration of the pulses, and 5) the total exposure time.